GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: January 24, 1977

Project Title: Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane

Project No: E-16-607

Co-Project Directors: Dr. Ben T. Zinn/Dr. Robert A. Cassanova

Sponsor: Olin Corporation

Agreement Period: From 2/1/77 Until 10/31/77

Type Agreement: Standard Industrial Research Agreement

Amount: $10,125

Reports Required: Quarterly Reports; Final Report

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

Dr. Charles A. Hofrichter
Urethane Chemicals Safety Director
Chemicals Group
Olin Corporation
275 Winchester Avenue
New Haven, Connecticut 06054

Defense Priority Rating: None

Assigned to: Aerospace Engineering (School/Laboratory)

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Other

CA-3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: May 23, 1978

Project Title: Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane

Project No: E-16-607

Project Director: B. T. Zinn

Sponsor: Olin Corporation

Effective Termination Date: 12/31/77

Clearance of Accounting Charges: 12/31/77

Grant/Contract Closeout Actions Remaining:

- x Final Invoice ~~and Closing Documents~~
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

Assigned to: Aerospace Engineering (School/Laboratory)

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CA—4 (3/76)

E-16-607

OLIN CHEMICALS GROUP

RESEARCH PROJECT NUMBER E16-607

MEASUREMENT OF THE CHARACTERISTICS OF SMOKE GENERATED BY A SMOLDERING POLYURETHANE

Quarterly Progress Report

for the period

February 1, 1977 to April 30, 1977

Co-Principal Investigators: Dr. B. T. Zinn, Regents' Professor

Dr. R. A. Cassanova, Senior Research Engineer

Other Personnel: Dr. R. F. Browner, Assistant Professor of Chemistry, School of Chemistry

School of Aerospace Engineering

Georgia Institute of Technology

Atlanta, Georgia

INTRODUCTION

This quarterly report describes the results of tests which were conducted under Olin Chemicals Group research project number E16-607 during the period February 1, 1977 to April 30, 1977. The contract under consideration is entitled "Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane." The objective of this study is the measurement of the physical properties of the smoke particulates and of the amounts of HCl, HCN and aldehydes contained in the particulates generated during non-flaming combustion of a rigid polyurethane sample. The tests are being conducted in the Georgia Tech Combustion Products Test Chamber.

COMPOSITION OF POLYURETHANE SAMPLE

The material being tested under this program is a rigid polyurethane foam which is designated as Olin RF-230. Samples of the foam were delivered to Georgia Tech by Dr. C. H. Hofrichter on February 23, 1977.

MEASUREMENT OF THE PHYSICAL CHARACTERISTICS OF THE SMOKE AT 25°C and 125°C

The series of tests conducted during the last quarter was concerned with the measurement of the smoke particle size characteristics, optical density and concentration when the samples are exposed to 2.5 Watts/cm^2 and 10 Watts/cm^2 radiant heat flux at environmental air temperatures of 25°C and 125°C. Results of a test with a heat flux of 5 Watts/cm^2 at 25°C are also reported. The particle sampling instruments and the in situ optical system were utilized in the 25°C tests, but only the in situ optical system was utilized in the 125°C tests. Complete data are not reported herein for the tests conducted at 2.5 Watts/cm^2 since the generated smoke concentrations

were too low for the instruments to measure. All tests at 2.5 Watts/cm^2 and 10 Watts/cm^2 were conducted with a flowrate of 15 cfm through the CPTC. This flowrate has been the "standard" flowrate for most of the previous tests in the CPTC which were funded by the National Science Foundation and the Products Research Committee. The same flowrate was utilized in these initial tests in order to facilitate a direct comparison of the results obtained under the above-mentioned NSF and PRC research programs.

Weight Loss Data

Figure 1 summarizes the weight loss data. The 2.5 Watts/cm^2 data at 25°C air temperature shows a very gradual weight loss throughout the test with a final weight loss of about 15%. The 5 Watts/cm^2 data at 25°C indicates a much faster weight loss rate early in the test; however, the total weight loss is only 28% of the original weight. The 10 Watts/cm^2 data at 25°C and 125°C shows very high weight loss rates during the first two minutes of the test. However, the char which remained at 6 minutes of exposure to 10 Watts/cm^2 heat flux was about the same for the 25°C and 125°C air temperatures.

Smoke Particle Mass Concentration at 25°C

Figure 2 shows the mass concentration data which were measured at 5 and 10 Watts/cm^2. The 2.5 Watts/cm^2 test did not produce a measurable concentration at the standard CPTC test flowrate of 15 cfm. As would be expected from the weight loss data in Figure 1, the 10 Watts/cm^2 condition produced a significantly greater concentration of particulate mass.

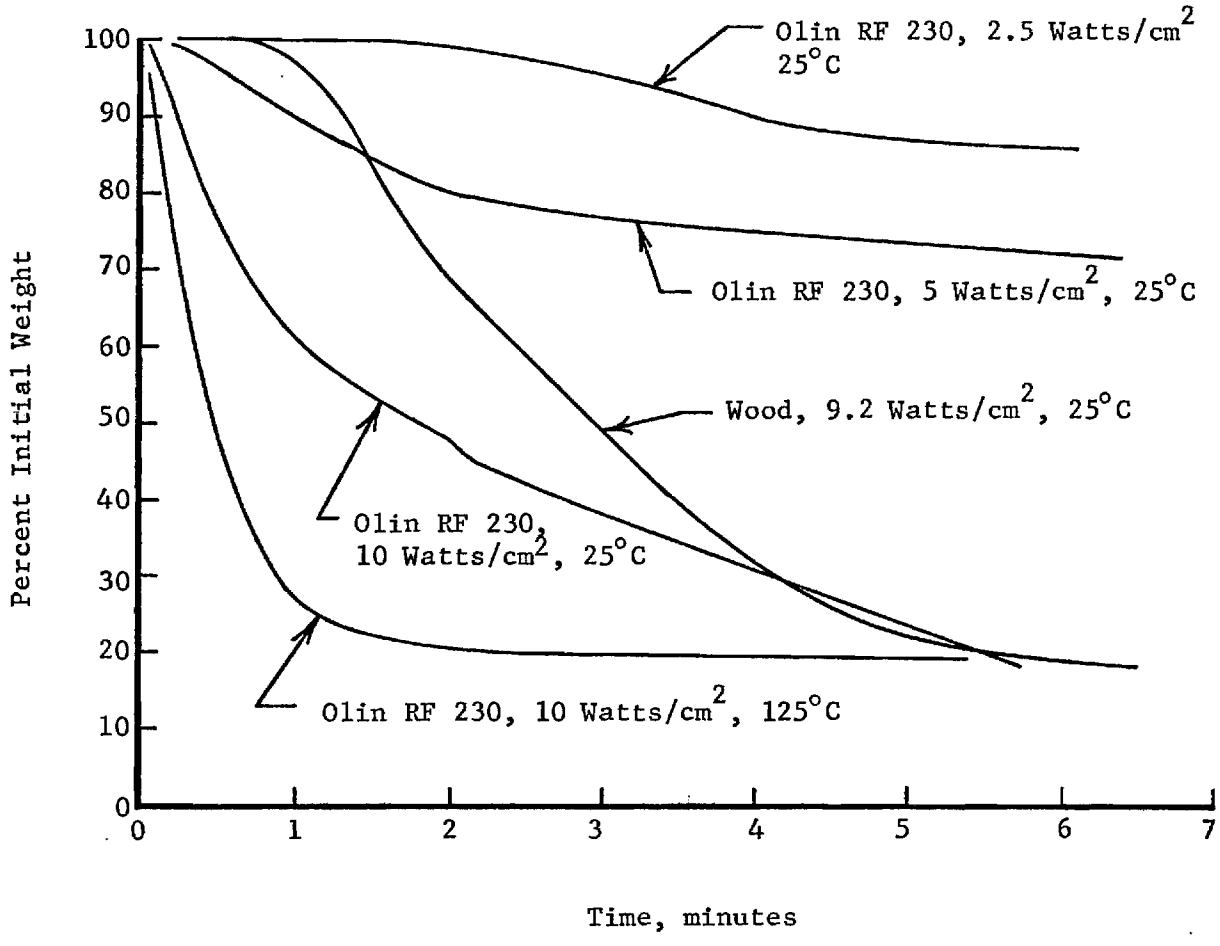


Figure 1. Sample Weight Loss Data

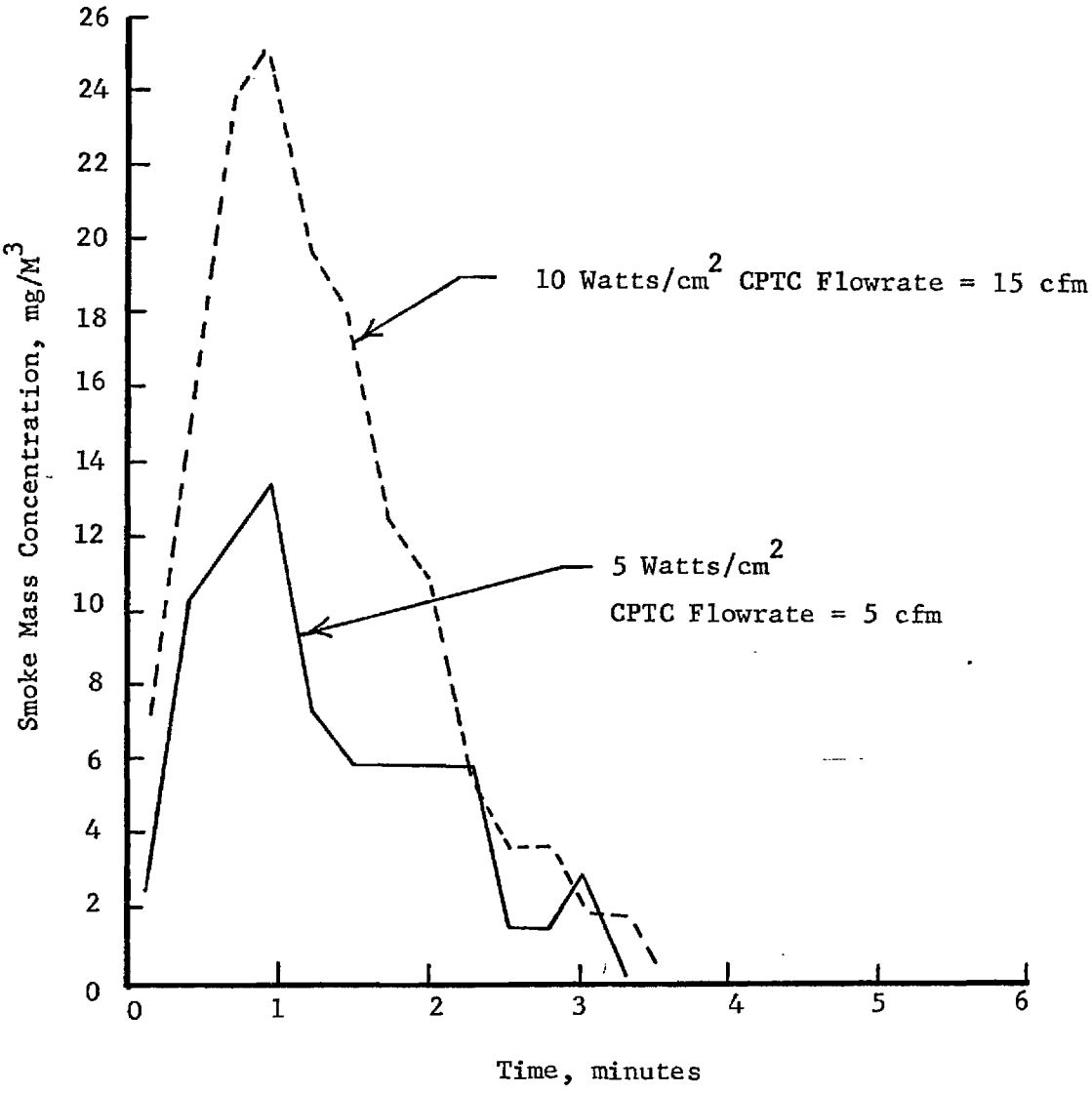


Figure 2. Smoke Particle Mass Concentration

Smoke Particle Size Distributions at 25°C

The smoke particle size distribution which was obtained with the cascade impactor for the 10 Watts/cm^2 condition is shown in Figure 3. The smoke is sampled continuously over the entire test time; thus, the resulting size distribution is an integrated distribution for the entire test. This type of data also gives a quantitative indication of the total particulate matter generated by the sample. The 2.5 and 5 Watts/cm^2 test conditions produced only trace amounts of particulate deposits on the cascade plates and it cannot be reported. Also included in the figure are data from previous tests of wood at 9.2 Watts/cm^2. The slight difference in heating rate for the wood sample is not likely to alter the test results. It should be noted that the wood ignited at approximately one minute into the test; whereas the Olin RF 230 sample did not; so that a direct comparison of the two materials under completely smoldering conditions at 10 Watts/cm^2 is not possible. The RF 230 produced more particulate weight per gram of sample weight than did the wood at this test condtion. Both materials produced particles with sizes in the range of about .4 microns to 4 microns.

Figures 4 and 5 show the size distribution data obtained using the Whitby Analyzer in tests utilizing 5 Watts/cm^2 and 10 Watts/cm^2 heat fluxes, respectively. Both test conditions produced particles with high particle concentrations below the size of one micron at the indicated test times. Reliable data is not available earlier in the test since in the early portion of each test the particulate concentration was increasing rapidly during the scan time. Size distributions at times later than indicated are not available because the particulate concentration was too low.

The corresponding size distribution for 10 Watts/cm^2 obtained with the cascade impactor which is shown in Figure 3 indicates significant particulate

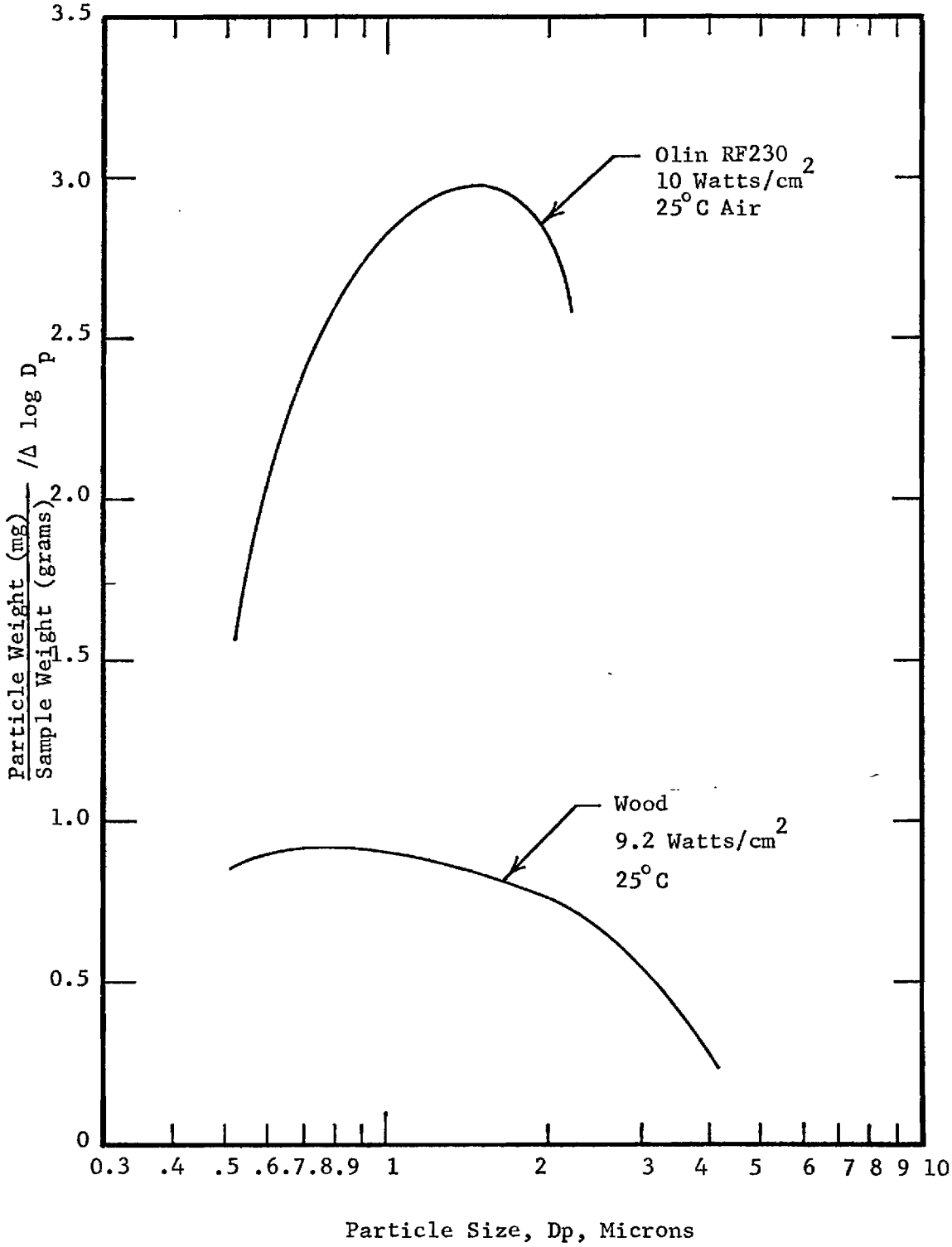


Figure 3. Comparison of Particle Size Distributions Measured for Olin RF 230 and Wood

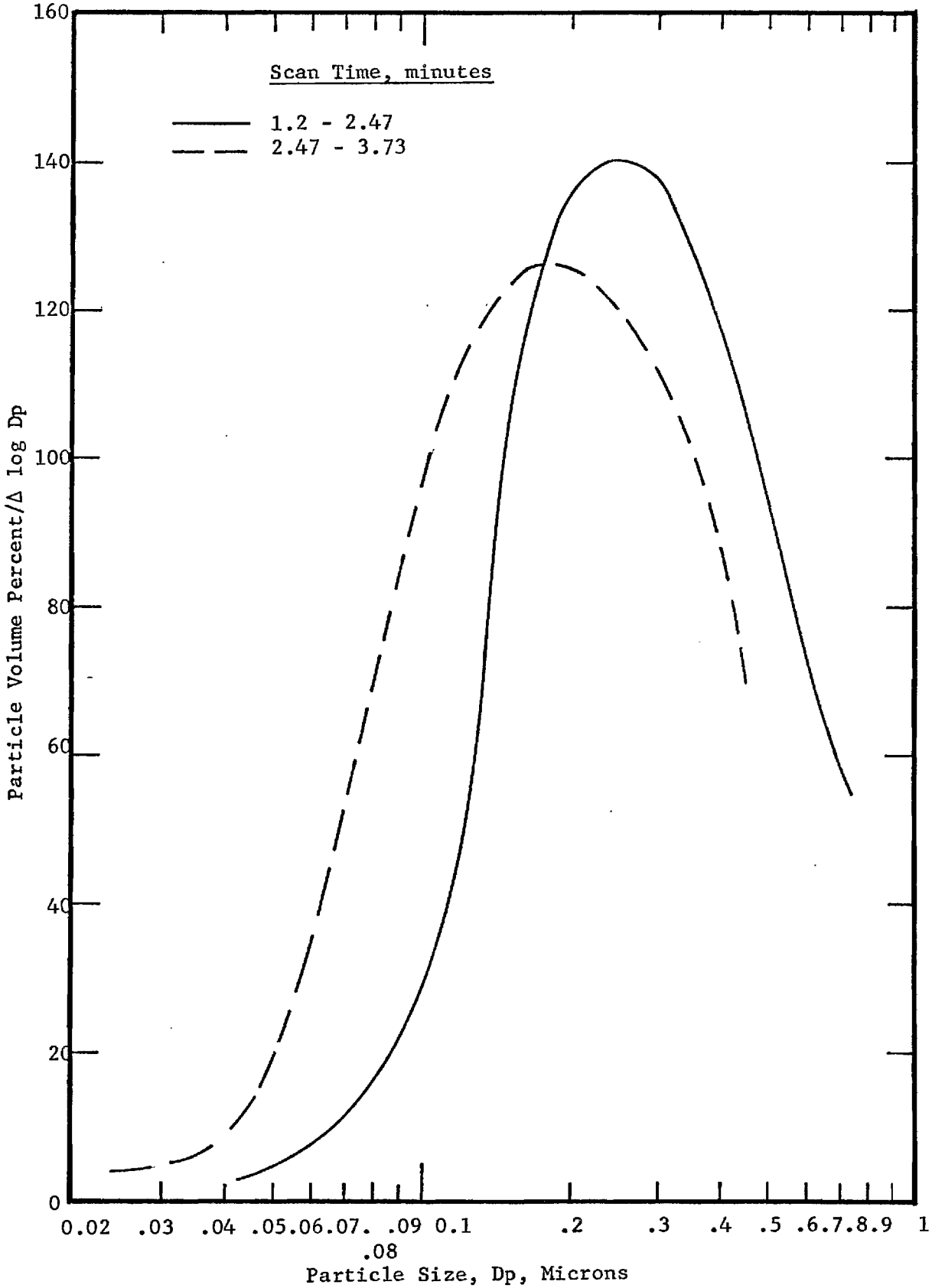


Figure 4. Particle Size Distributions Measured for Olin RF230 Exposed to 5 Watts/cm^2 Radiant Flux and 25°C Air

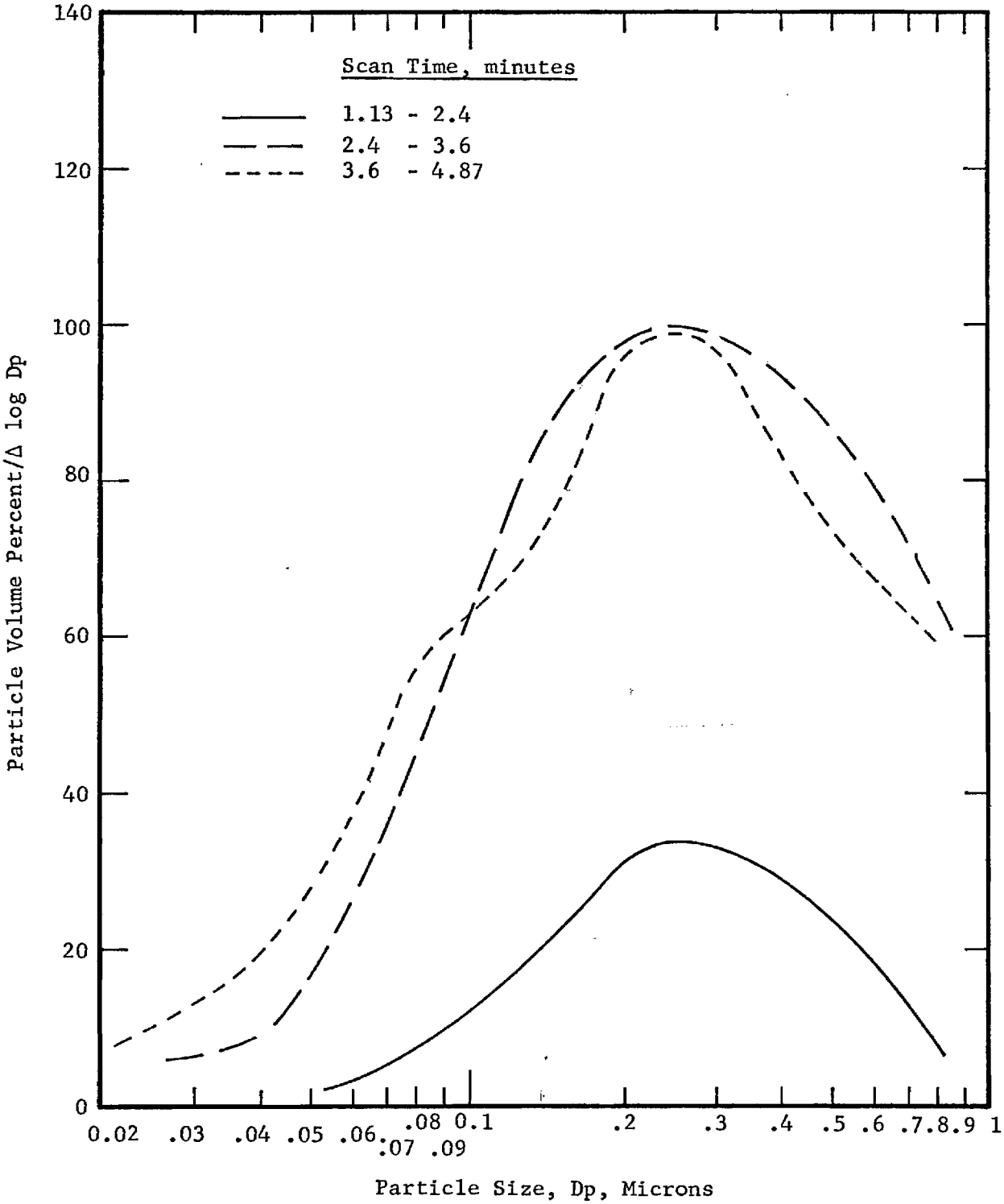


Figure 5. Particle Size Distributions Measured for Olin RF 230 Exposed to 10 Watts/cm^2 Radiant Flux and 25°C Air

concentrations above one micron. However, this cascade impactor data does not contradict the EAA data since the impactor collects most of the particulate matter during the early stages of the test when the concentration is high and the particles would tend to be large.

Optical Density and Average Particle Size

The optical density measurements in the 25°C environmental air temperature at 5 Watts/cm^2 and 10 Watts/cm^2 are presented in Figure 6. The 10 Watts/cm^2 heat flux produced significantly greater optical densities than the 5 Watts/cm^2 while the 2.5 Watts/cm^2 heat flux did not produce a measurable optical density. Figure 7 shows a comparison of the effect of environmental temperature on the optical density for the 10 Watts/cm^2 heat flux. Increasing the CPTC ventilation gas temperature to 125°C reduced the maximum optical density to about one-half of the value which was measured at 25°C.

Figure 8 shows the variation of the average particle size during exposure of the sample to 5 and 10 Watts/cm^2 at an air temperature of 25°C. The average particle size during the tests in about 0.7 to 0.8 microns in both cases. Likewise, at the higher temperature of 125°C which is shown in Figure 9, the average particle size is also 0.8 microns before the concentration becomes too low for reliable measurements.

Chemical Analysis of the Combustion Products

Attempts were made to measure the amounts of CO and CO_2 in combustion products by withdrawing samples from the sampling section. The sample was drawn through a membrane filter to remove all of the particulate matter and then collected in a gas-tight, plastic sample bag. A gas syringe was then used to withdraw samples from the bag which were then injected onto the GC column. Typical results are shown in Figure 10. The polyurethane

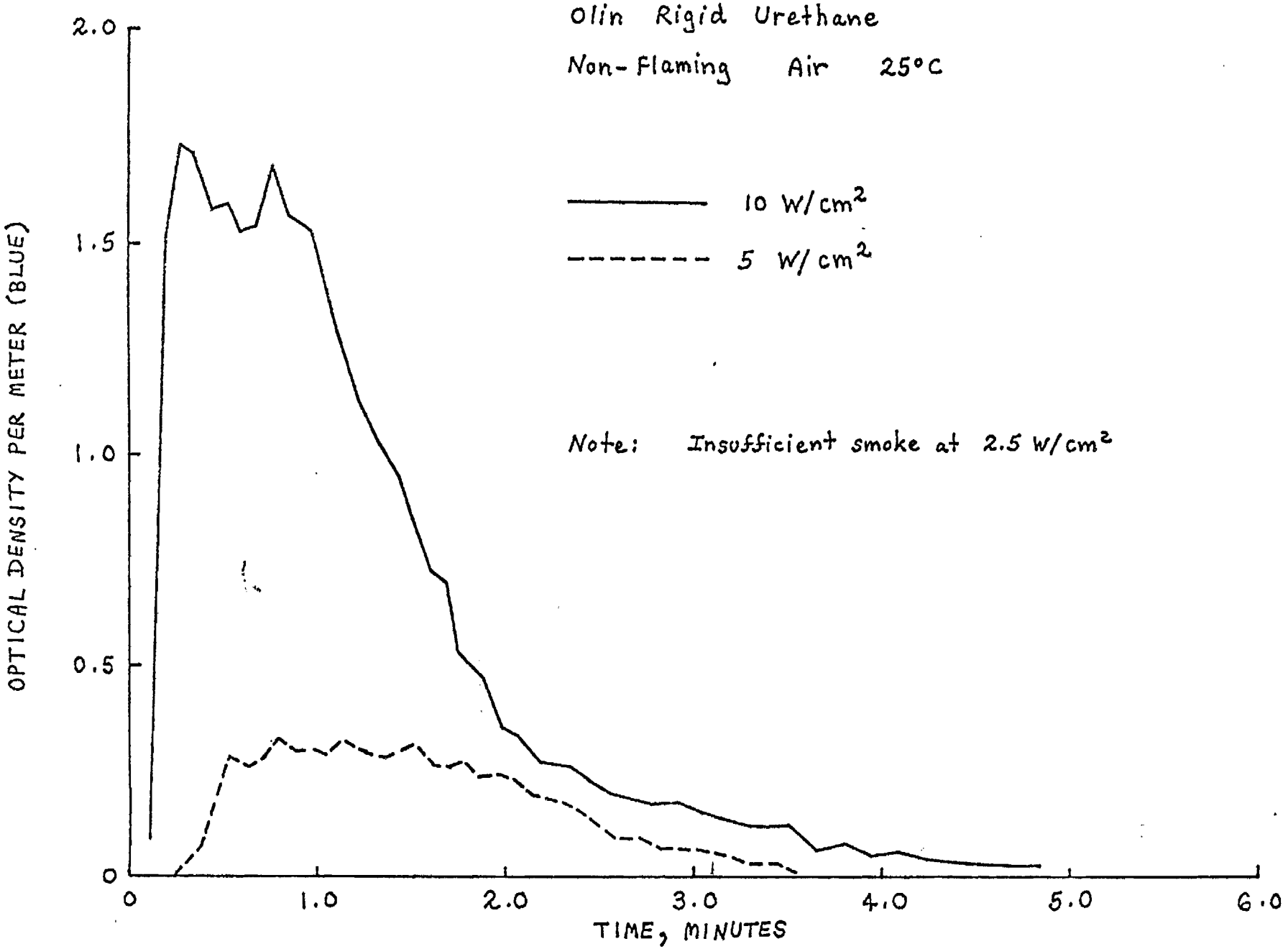


Figure 6. Optical Density at 5 and 10 Watts/cm^2 with 25°C Air Temperature

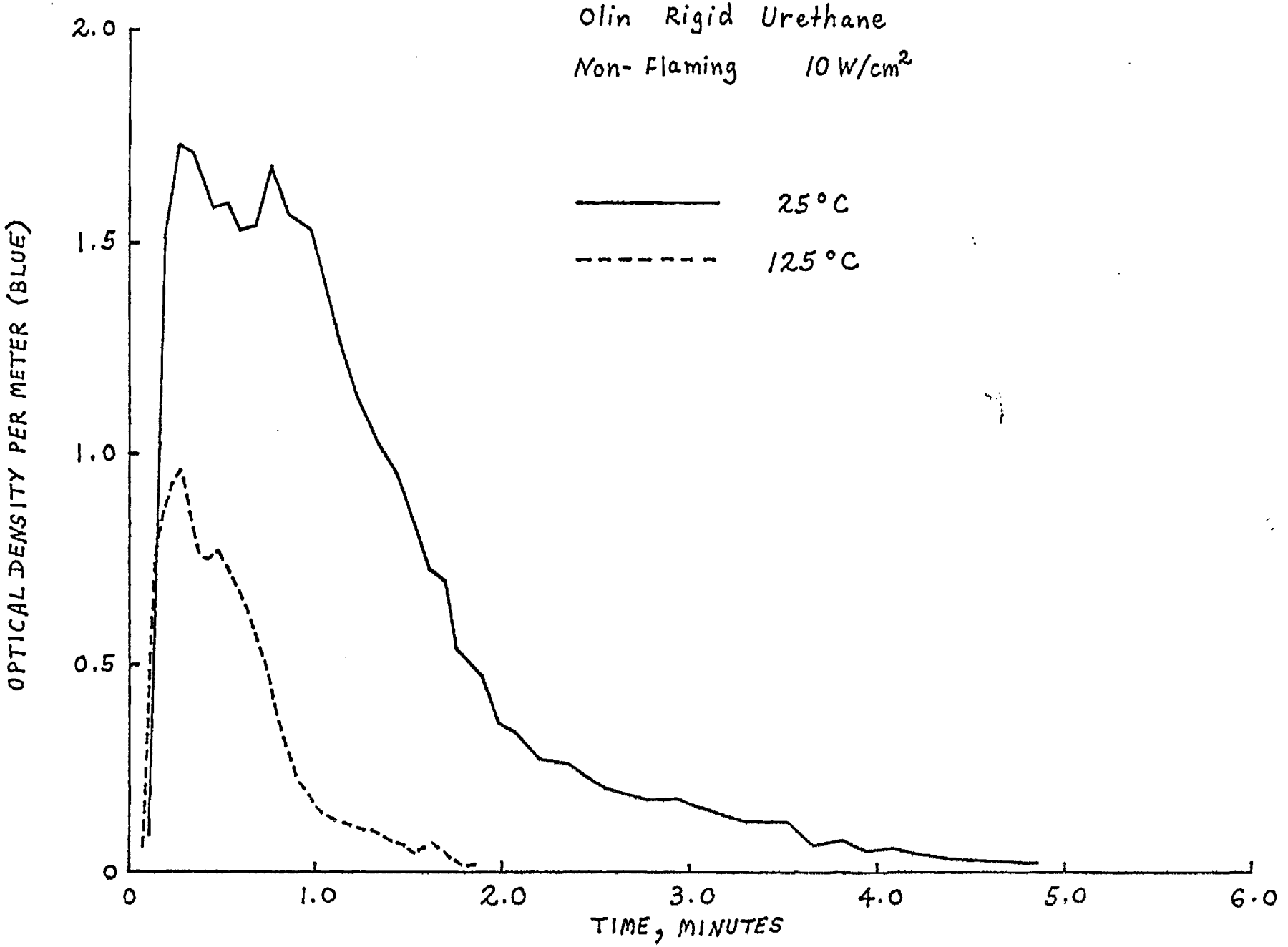


Figure 7. Optical Density at 10 Watts/cm^2 with 25°C and 125°C Air Temperature

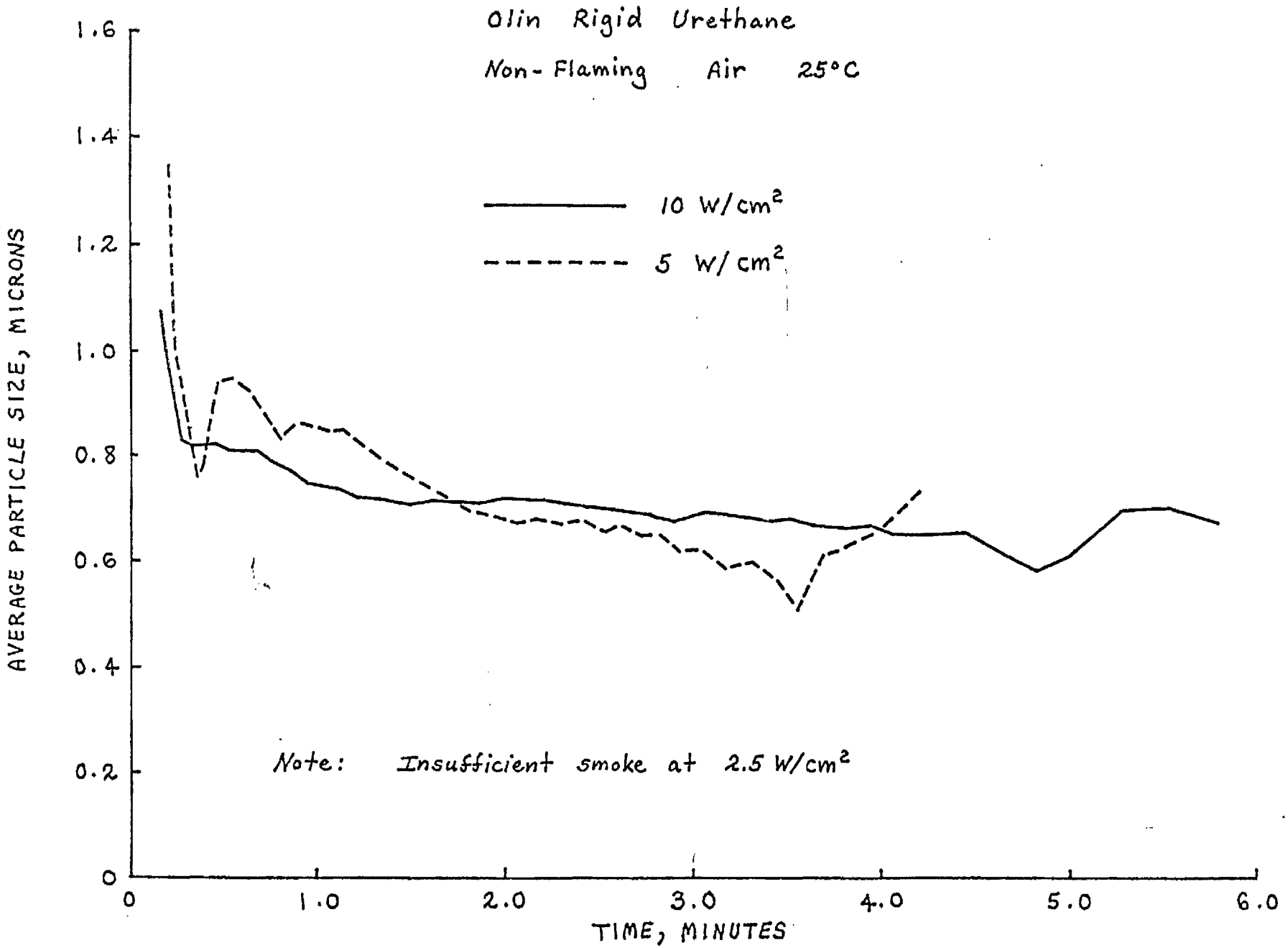


Figure 8. Average Particle Size at 5 and 10 Watts/cm^2 with 25° Air Temperature

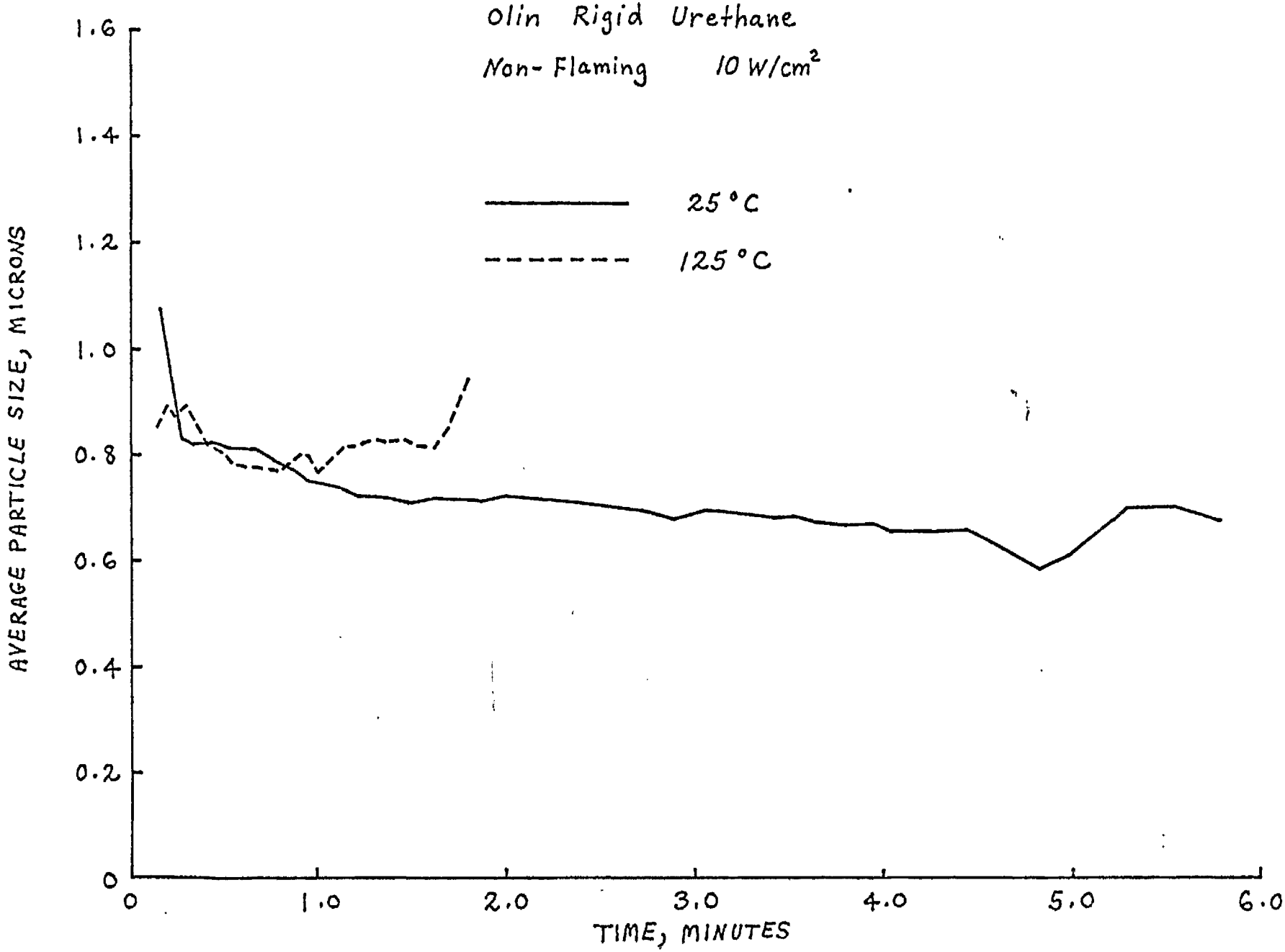


Figure 9. Average Particle Size at 10 Watts/cm^2 with 25°C and 125°C Air Temperature

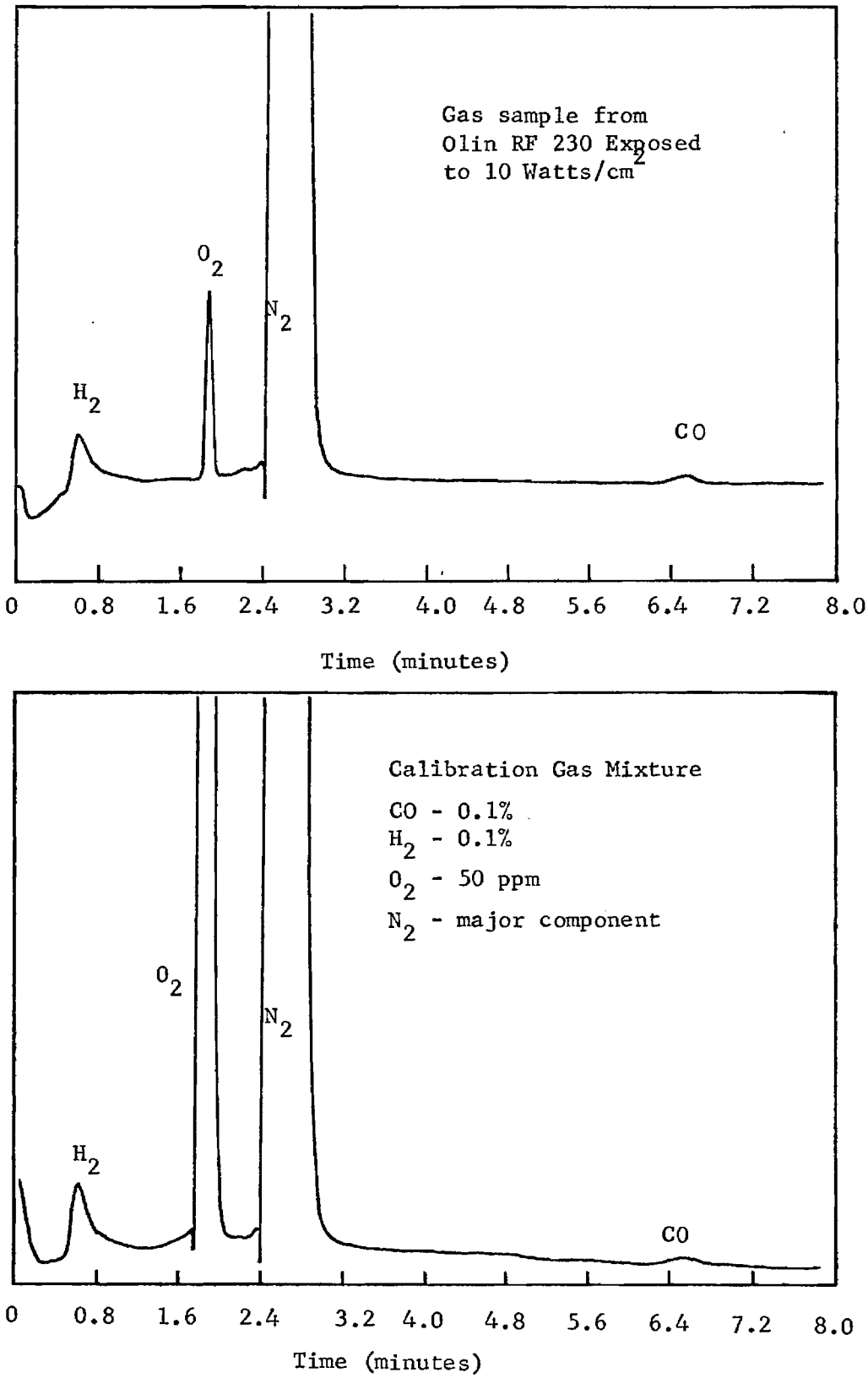


Figure 10. Gas Chromatogram of Gas Sample Collected from Smoldering Combustion of Olin RF 230.

was exposed to a 10 Watts/cm^2 heat flux at an air temperature of 25°C and a CPTC flowrate of 5 cfm. The collected sample chromatogram is compared with a calibration gas mixture chromatogram and shows that the peaks which are produced by the calibration CO and the sample CO are comparable, i.e., about 0.1% of the total. In view of this result, it appears that identification of the amounts of CO and CO_2 in the combustion products by using only the GC will be very difficult.

Work is continuing on the apparatus for collecting particulate samples for the identification of the HCl, HCN and aldehydeswhich are contained in the particulate matter.

Anticipated Modifications to the Test Procedures

Since the "standard" flowrate of 15 cfm dilutes the smoke to the extent that the smoke concentrations are too low for measurement at 2.5 Watts/cm^2 heat flux, the remaining tests at all of the proposed conditions will be conducted with a CPTC flowrate of 5 cfm. However, in view of the results which were obtained at 5 Watts/cm^2 and a CPTC flowrate of 5 cfm, it is doubtful that the smoke concentration which is produced at 2.5 Watts/cm^2 and a CPTC flowrate of 5 cfm will be sufficient for accurate measurements at the low CPTC air temperatures.

No further attempts will be made to measure the CO and CO_2 concentrations in the combustion products. The combined effects of small sample size, relatively large CPTC volume and the dilution of the combustion products by the CPTC ventilation flow make the quantitative analysis of the combustion gases very difficult with only the gas chromatograph. The combustion gases could be concentrated before attempting to identify the components, or a combined gas chromatograph/mass spectrometer technique could possibly be used. However, in view of the low concentrations, it is felt that the extra effort

would be better spent on developing the methodology for identifying the quantities of HCl, HCN and the aldehydes which are present in the particulates.

E-16-607

OLIN CHEMICALS GROUP

RESEARCH PROJECT NUMBER E16-607

MEASUREMENT OF THE CHARACTERISTICS OF SMOKE GENERATED BY A SMOLDERING POLYURETHANE

Quarterly Progress Report

for the period

May 1, 1977 to July 31, 1977

Co-Principal Investigators: Dr. B. T. Zinn, Regents' Professor

Dr. R. A. Cassanova, Senior Research Engineer

Other Personnel: Dr. R. F. Browner, Assistant Professor of Chemistry, School of Chemistry

School of Aerospace Engineering

Georgia Institute of Technology

Atlanta, Georgia

INTRODUCTION

This quarterly report describes the results of tests which were conducted under Olin Chemicals Group research project number E-16-607 during the period May 1, 1977 to July 31, 1977. The contract under consideration is entitled "Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane." The objective of this study is the measurement of the physical properties of the smoke particulates and of the amounts of HCl, HCN and aldehydes contained in the particulates generated during nonflaming combustion of a rigid polyurethane sample. The tests are being conducted in the Georgia Tech Combustion Products Test Chamber.

MEASUREMENT OF THE PHYSICAL CHARACTERISTICS OF THE SMOKE AT 200°C

High temperature (200°C) tests were conducted in the Combustion Products Test Chamber at 2.5 W/cm^2 and 10 W/cm^2. Figure 1 compares the weight loss data which was obtained at 200°C with the weight loss measured at 25°C and 125°C. The data which is indicated for the 2.5 W/cm^2 case is estimated based on the initial and final sample weights for this test. The force transducer did not operate properly for this test. However, in comparison with the previously reported 25°C weight loss data, the 200°C data showed only a slightly higher weight loss. The 10 W/cm^2 data for 200°C indicates essentially the same weight loss which was previously reported for the 125°C case.

Smoke optical density measurements shown in Figure 2 indicate that increasing the ventilation gas temperature to 200°C with a radiant heat flux of 10 W/cm^2 had the effect of reducing the optical density as compared to the 25°C and 125°C cases. The corresponding average particle size measurements shown in Figure 3 indicates that the average particle size stabilized at about 0.7 microns after

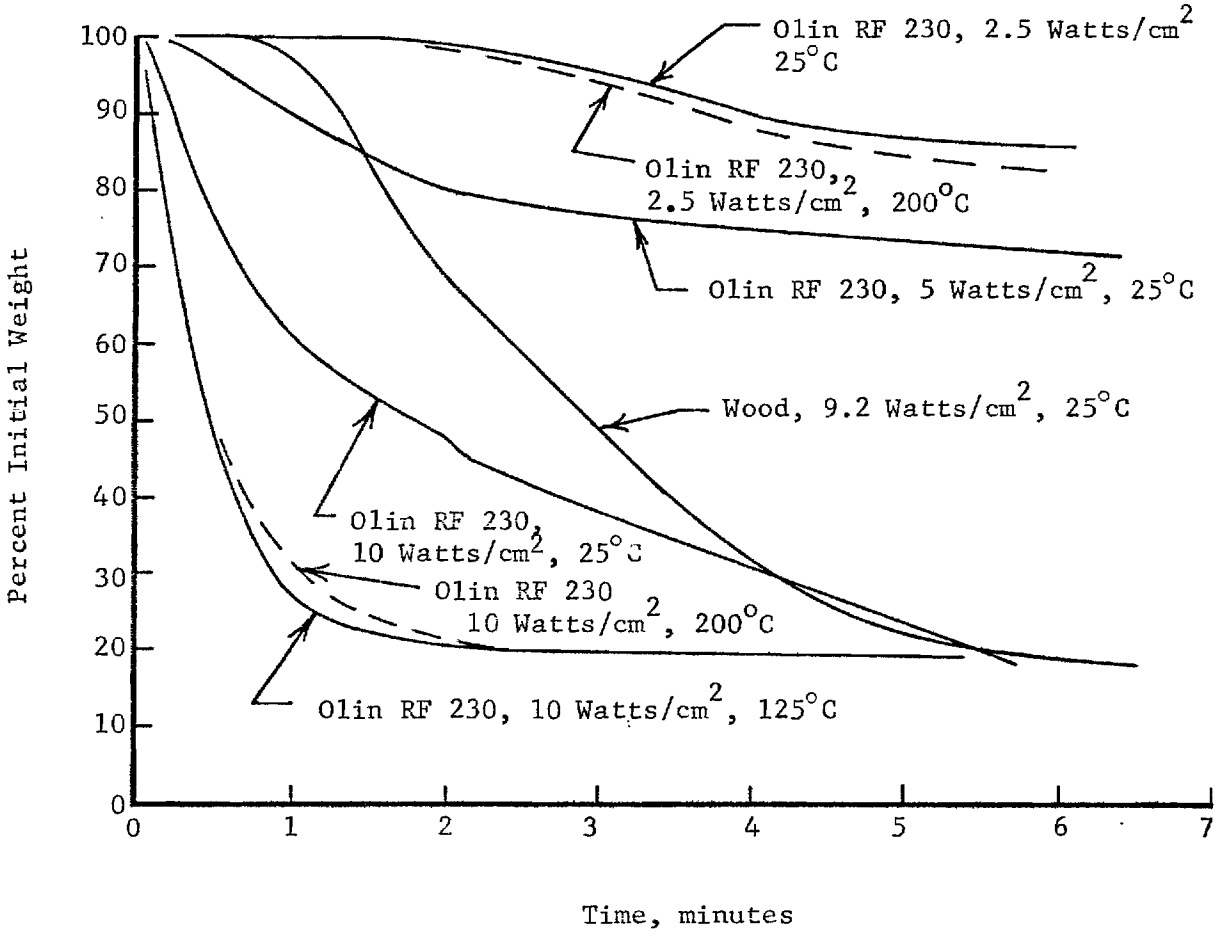


Figure 1. Sample Weight Loss Data

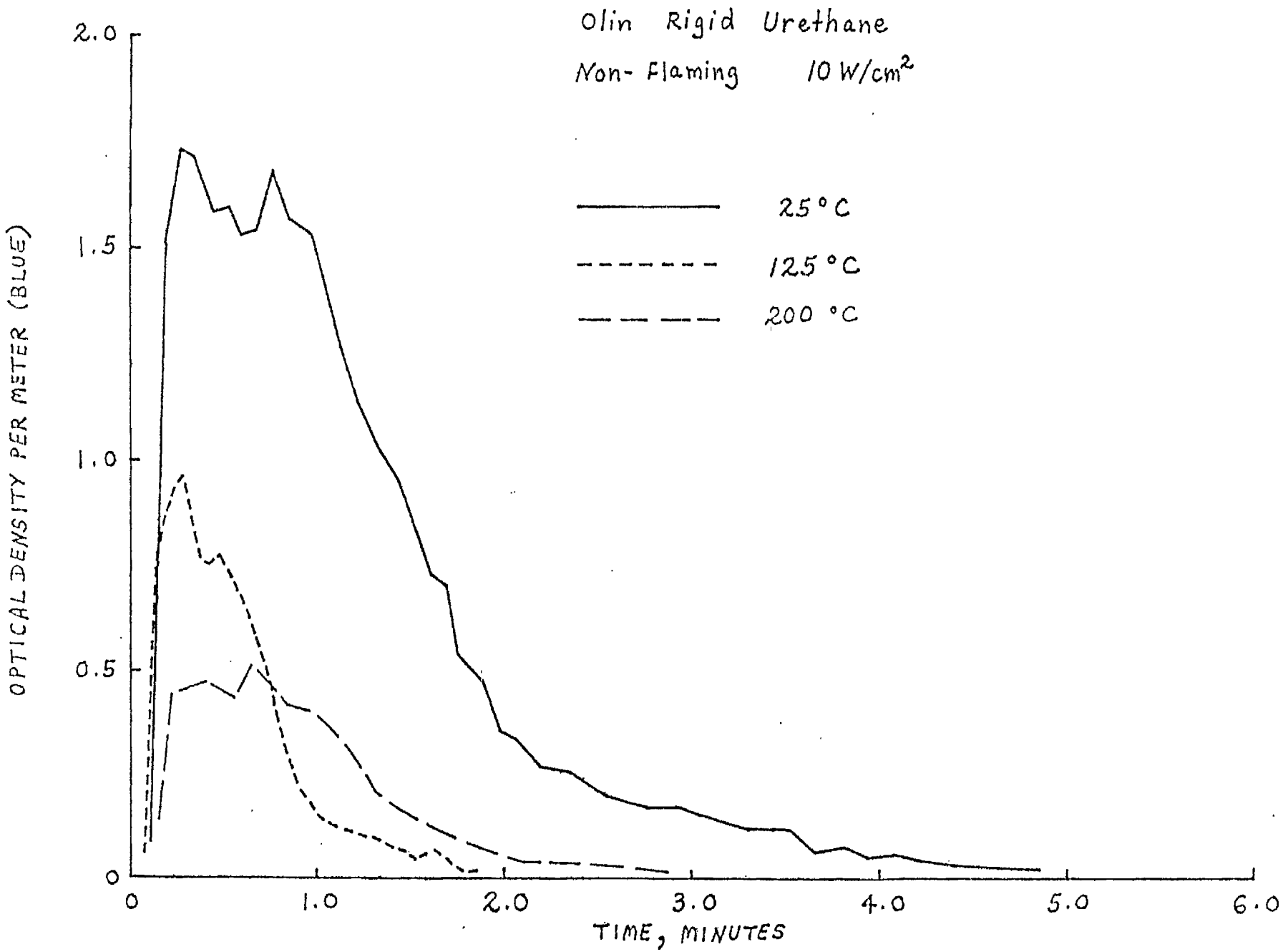


Figure 2. Optical Density at 10 W/cm^2 with 25°C, 125°C and 200°C Ventilation Air Temperatures.

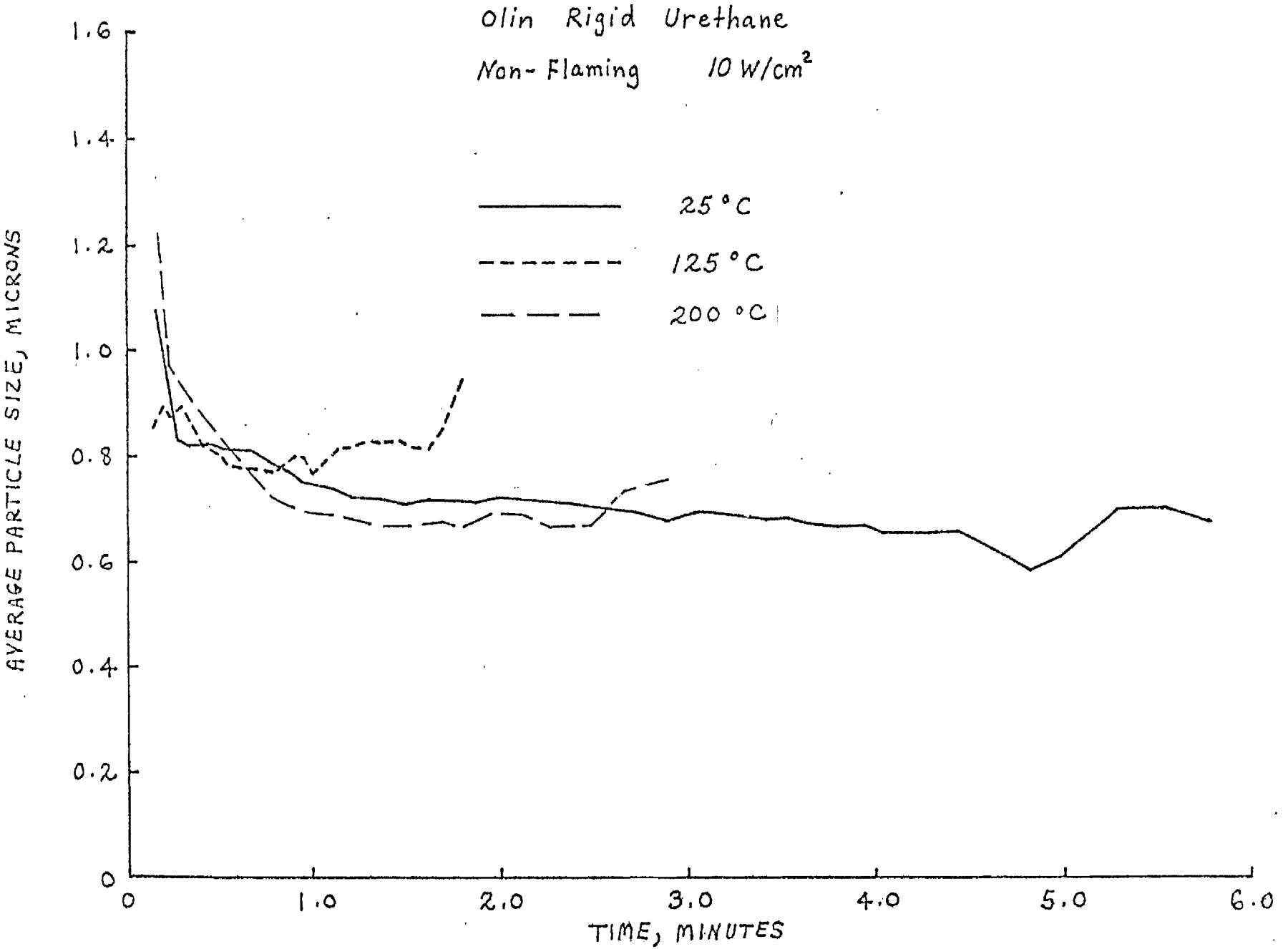


Figure 3. Average Particle Size at 10 W/cm^2 with 25°C, 125°C and 200°C Ventilation Air Temperatures.

the initial starting transient for all three ventilation gas temperatures. Data is not reported for a radiant heat flux of 2.5 W/cm^2 since the smoke concentration was too low to be measured by the in situ optical system.

MEASUREMENT OF HCl, HCN AND ALDEHYDES IN THE PARTICULATES

The apparatus for collection and separation of the absorbed gases in the particulate matter was completed during this quarter and preliminary separations were completed. Figure 4 shows the apparatus for desorbing the gases and low molecular weight volatiles from the particulates. The smoke particles are first collected on the filter media by drawing the combustion products through the filter with a vacuum pump. The filter holder is then attached as shown in Figure 4. The filter holder is then warmed to 50°C at which time the helium is flowed through the filter and into the sample collection tube at a rate of 40 ml/min for 25 minutes. The HCl, HCN and Aldehydes are trapped in the sample collection tube which is packed with Porapak R. The sample collection tube is then transferred to the apparatus shown in Figure 5 which is a modification to the inlet system of the HP5720-A gas chromatograph. The collection tube is heated to 200°C at which time the helium gas flow is switched to position B for 2 minutes and the cut-off valve opened to allow the sample to be transferred into the injection port. At the end of 2 minutes the helium gas flow is switched to position A and the gas chromatograph temperature program is started. The gc column is at 65°C during the 2 minute injection period and then raised to 220°C at 8°C/min.

Figures 6 and 7 show the preliminary separations obtained by using the apparatus and techniques just described for particulates collected from wood and polyurethane combustion products. Both chromatograms indicate good separation of a number of compounds. Identification of the separated compounds

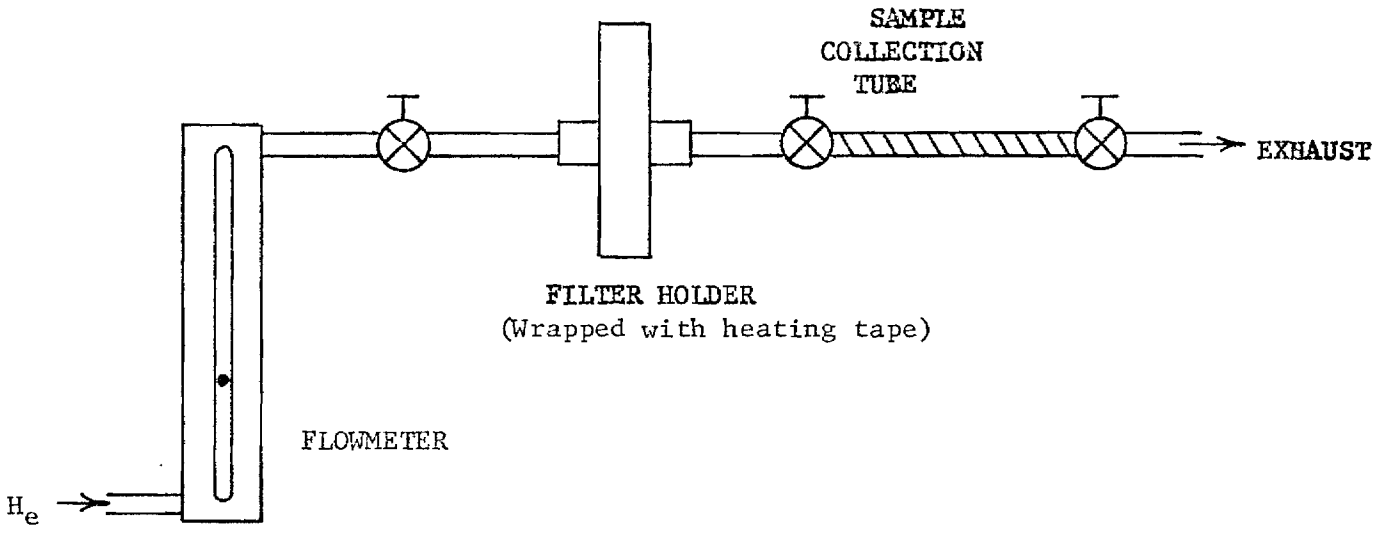


Figure 4. Apparatus for Sample Collection

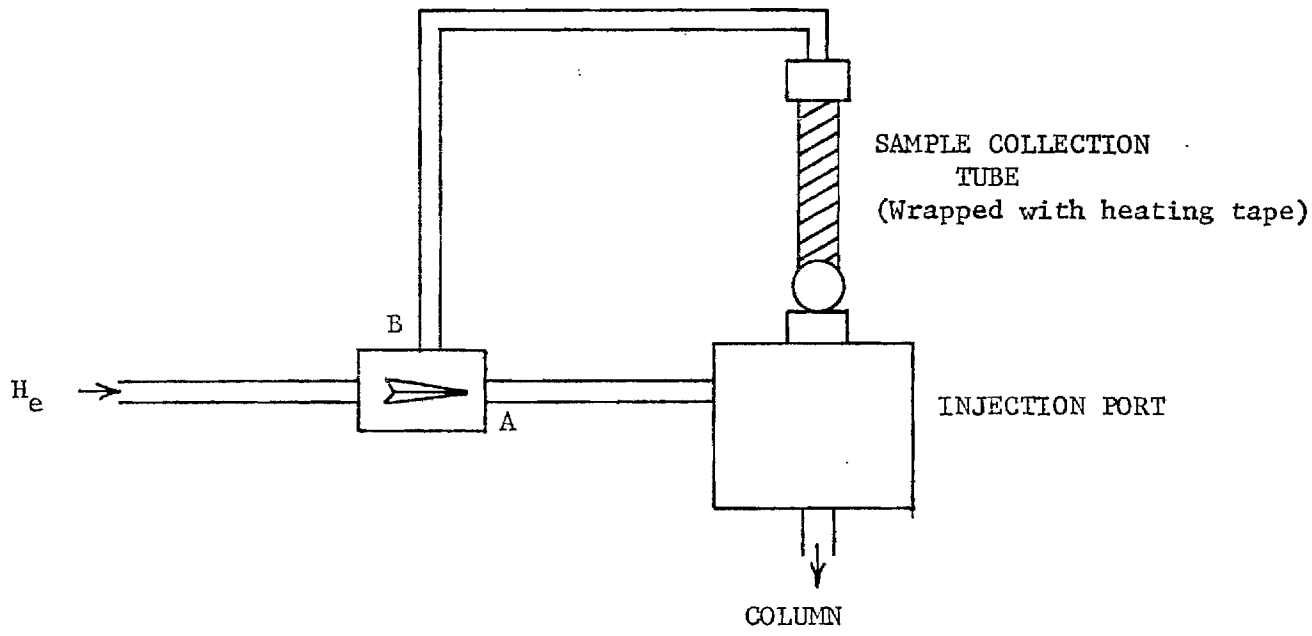


Figure 5. Sample Injection System.

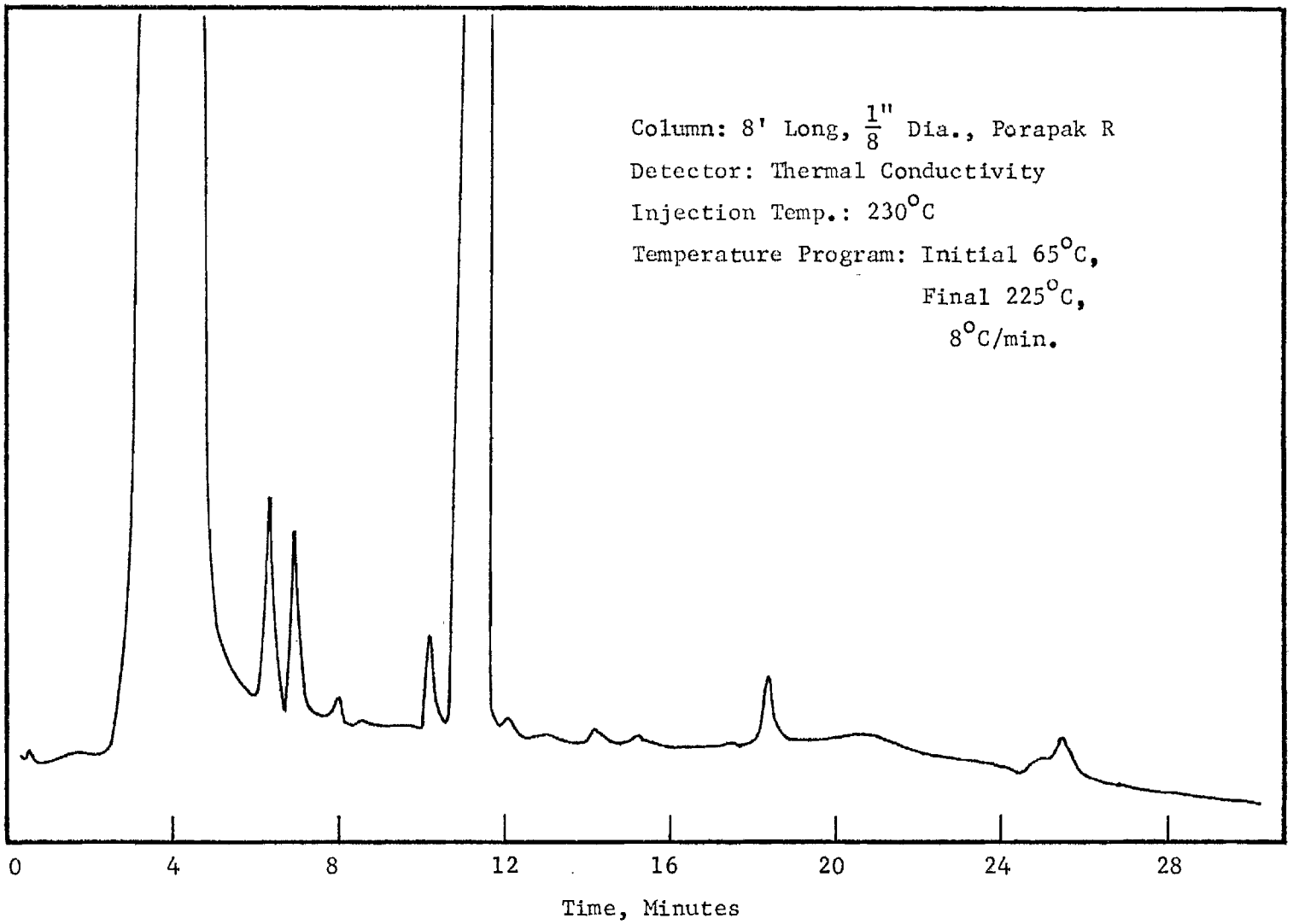


Figure 6. Gas Chromatogram of Sample Collected From the Combustion Products of a Smoldering Polyurethane.

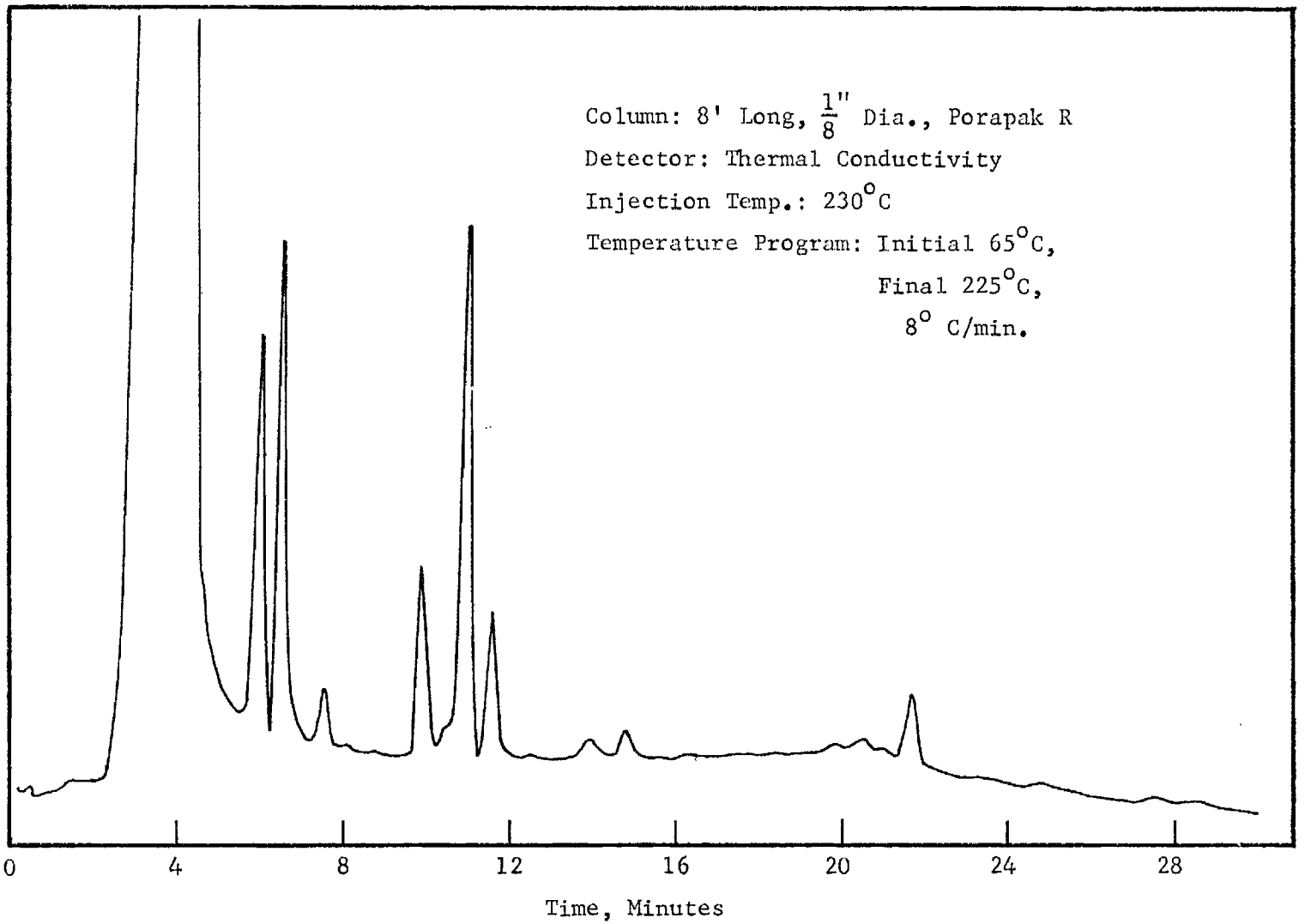


Figure 7. Gas Chromatogram of Sample Collected From the Combustion Products of Smoldering Wood.

will be by GC/MS techniques during the next quarter of the grant period. The gas chromatograph which is interfaced with the mass spectrometer is currently being modified with a sample injection system which was previously described.

E16-607

FINAL REPORT

MEASUREMENT OF THE CHARACTERISTICS OF SMOKE GENERATED BY A SMOLDERING POLYURETHANE

By

B. T. Zinn
R. A. Cassanova
R. F. Browner
C. P. Bankston
E. A. Powell
R. O. Gardner

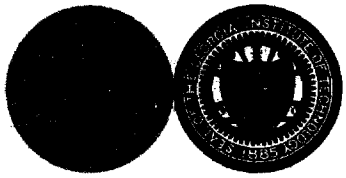
Prepared for

OLIN CORPORATION
NEW HAVEN, CONN. 06504

For the period February 1, 1977 to December 31, 1977

January 1978

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF AEROSPACE ENGINEERING
ATLANTA, GEORGIA 30332



MEASUREMENT OF THE CHARACTERISTICS OF SMOKE GENERATED BY A SMOLDERING POLYURETHANE

B. T. Zinn, Regents' Professor
R. A. Cassanova, Sr. Research Engineer

R. F. Browner, Assistant Professor
C. P. Bankston, Research Engineer
E. A. Powell, Assistant Professor
R. O. Gardner, Graduate Research Assistant

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Final Report to the Olin Chemicals Group
for the period

February 1, 1977 to December 31, 1977

ABSTRACT

This report describes the research conducted under an Olin Chemicals Group research project entitled "Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane." Measurements have been made of the physical properties of the smoke particulates generated by combusting Olin rigid polyurethane foam RF-230 under nonflaming conditions at three radiant heating rates and four ventilation gas(air) temperatures. Results show that sample decomposition rates and particulate concentrations increase, and char fraction remaining decreases with increasing radiant heating rate in a room temperature environment. As the ventilation gas (environmental) temperature increases, sample decomposition rates are observed to monotonically increase for a given radiant heating rate. The effects of increasing ventilation temperature on smoke physical properties, however, depend upon the radiant heating rate under consideration. Chemical analysis of the volatile compounds absorbed onto the smoke particulates generated by the RF-230 foam (nonflaming) resulted in the identification of several organic compounds. However, no positive identification of HCN or low molecular weight aldehydes was achieved at the level of sensitivity of the sampling and analysis system utilized in this study.

TABLE OF CONTENTS

I. INTRODUCTION

This report describes the results of tests which were conducted under Olin Chemicals Group research project number E-16-607 during the period February 1, 1977 to November 1, 1977. The contract under consideration is entitled "Measurement of the Characteristics of Smoke Generated by a Smoldering Polyurethane." The objective of this study is the measurement of the physical properties of the smoke particulates and of the amounts of HCl, HCN and aldehydes contained in the particulates generated during non-flaming combustion of a rigid polyurethane sample under different environmental conditions. This program has been directed by Drs. Ben T. Zinn and Robert A. Cassanova in the School of Aerospace Engineering of the Georgia Institute of Technology. Other contributing professional personnel are Drs. R. F. Browner, C. P. Bankston and E. A. Powell. Also assisting is Mr. R. O. Gardner, Graduate Research Assistant.

II. EXPERIMENTAL FACILITIES

The smoke research program described herein has been conducted utilizing the following facilities which have been developed at the School of Aerospace Engineering, Georgia Institute of Technology: (1) A Combustion Products Test Chamber, (2) A Combustion Products Sampling System; (3) An In Situ Optical Aerosol Measurement System; and (4) A Chemical Analysis Laboratory.

The ventilated Combustion Products Test Chamber (CPTC) is capable of simulating a wide variety of environmental conditions that may be encountered in actual fire situations. Specifically, the design of the CPTC permits easy control and measurement of the following variables during the combustion of small samples of materials: (1) The mode of combustion (i.e., flaming vs. smoldering combustion); (2) The sample radiant heating rate (up to 10 W/cm^2); (3) The sample weight loss during the test; (4) The composition of the ventilating gas surrounding the sample; (5) The temperature of the ventilation gas (up to $650^{o}C$) and; (6) An option to test the sample under either vertical or horizontal mounting. A complete description of the CPTC including operating procedures, can be found in References 1 and 2.

During testing, a Combustion Products Sampling System is used to analyze smoke samples that are continuously withdrawn from the gases flowing from the CPTC. Information obtained by the Aerosol Sampling System includes particle size distributions and total particulate mass generated. In addition, collected smoke samples are retained for chemical analysis. A description of the sampling system can also be found in References 1 and 2.

In addition to the data obtained by sampling techniques, an In Situ Optical Aerosol Measurement System is utilized to make simultaneous mean particle size and concentration measurements. With this optical smoke analy-

sis system measurements of scattered blue light at forward angles of 5^{o} and 15^{o} and measurements of transmitted red and blue laser lights provide time resolved data describing the average size, volume concentration of the smoke particles, their index of refraction, and their optical density. Details of the optical system are available in References 2 and 3.

An on-line data acquisition system utilizing a Hewlett-Packard 2100 minicomputer is being used for acquiring, reducing and plotting all of the optical and sampling data with the exception of Andersen Sampler (cascade impactor) data which calls for the weighing of the samples collected on the various impaction plates.

Finally, a chemical laboratory containing analytical equipment for the chemical analysis of smoke particulates sampled during tests in the CPTC has been developed. The available equipment includes a high pressure liquid chromatograph, an infrared spectrophotometer, a gas chromatograph equipped with a thermal conductivity detector and a gas chromatograph which is equipped with dual flame ionization detectors and is interfaced to a mass spectrometer. The gas chromatograph/mass spectrometer system is also equipped with a computerized data acquisition and analysis system that records the total-ion chromatograms and the mass spectra.

III. TEST PROTOCOL

A. Sample Composition

The material being tested under this program is a rigid polyurethane foam which is designated as Olin RF-230. Samples of the foam were delivered to Georgia Tech by Dr. C. H. Hofrichter on February 23, 1977.

B. Test Conditions and Physical Properties Measured

The rigid polyurethane foam (Olin RF-230) was tested under the conditions outlined in Table I. These conditions were selected as representative of a range of environmental extremes which may be encountered in actual fire situations. All samples were mounted in the vertical position and the CPTC ventilation gas was composed of air flowing at 425 liters per minute in all tests, except for those tests conducted at 2.5 W/cm^2 when the flow rate utilized was 142 liters per minute. Finally, the average sample dimensions are 75 mm x 75 mm (exposed surface) x 15 mm thick, which correspond to sample weights of approximately 3.5 grams.

For the test conditions characterized by room temperature ($25^{o}C$) ventilation gases, data are available for the following measured quantities: (1) particle size distribution; (2) particulate mass generated; (3) the evolution of the mean particle diameter with time; (4) the variation of the smoke optical density (at 458 nm) with time, and (5) the sample mass loss as a function of time. Where test conditions are characterized by high temperature ventilation gases, only in situ optical system data (items 3 and 4 above) are available, in addition to the sample weight loss measurements. The aerosol sampling system instrumentation cannot be operated at elevated temperatures.

TEST NO.	VENTILATION GAS (AIR) TEMPERATURE ^{o}C	RADIANT HEATING LEVEL, W/cm^2
1	25	2.5
2	25	10
3	125	2.5
4	125	10
5	200	2.5
6	200	10
7	300	2.5
8	300	10

Table I. Sample Test Schedule

IV. RESULTS OF NONFLAMING TESTS OF OLIN RF-230 RIGID URETHANE FOAM-PHYSICAL PROPERTIES DATA

A. Low Temperature Tests at 2.5 W/cm^2 and 10 W/cm^2

Tests of Olin RF-230 rigid urethane samples under nonflaming conditions in a room temperature (25^{o}C) ventilation gas (air) have been completed. Measurements have been obtained of the characteristics of the smoke produced under nonflaming conditions at the previously specified 2.5 W/cm^2 and 10 W/cm^2 radiant heat fluxes. In addition, results of a test with a heat flux of 5 W/cm^2 at 25^{o}C are reported. These data are presented in Figures 1 through 6. However, not all of the 2.5 W/cm^2 tests produced useful data, since for the test conditions established in the CPTC (i.e., vertical sample mounting and continuous ventilation) the generated smoke concentrations were too low for the instruments to measure.

Figure 1 summarizes the weight loss data. The 2.5 W/cm^2 data show a very gradual weight loss throughout the test with a final weight loss of about 15%. The 5 W/cm^2 data at 25^{o}C indicate a much faster weight loss rate early in the test; however, the total weight loss is only 28% of the original weight. The 10 W/cm^2 data show very high weight loss rates during the first two minutes of the test, and a considerably greater total weight loss after 6 minutes of exposure. For reference purposes, the weight loss data [4] for wood samples exposed to 5 W/cm^2 and 9.2 W/cm^2 are also plotted in Figure 1. Note, however, that the wood sample subjected to 9.2 W/cm^2 radiant flux experienced flaming ignition between one and two minutes into the test.[1,4]

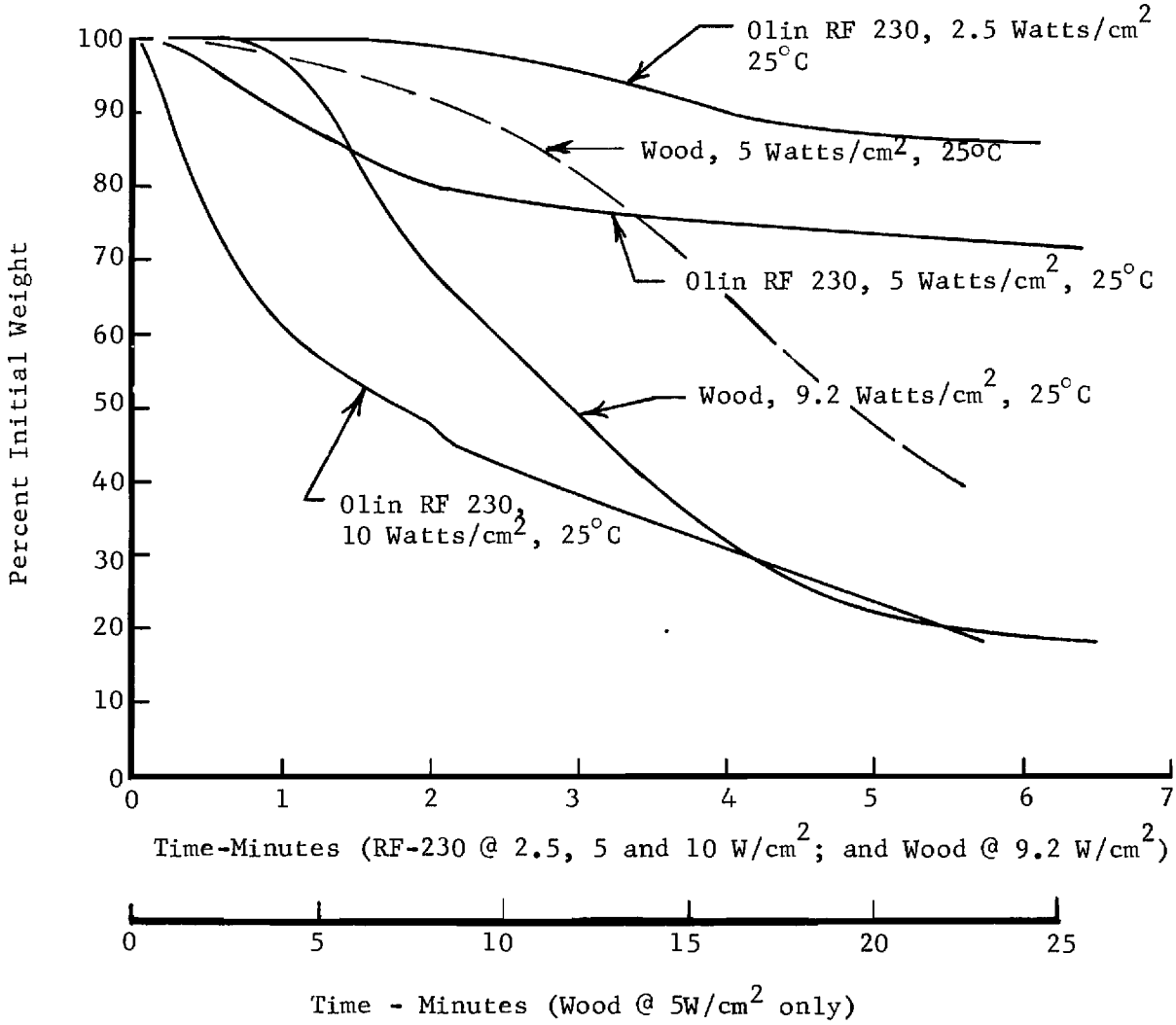


Figure 1. Olin RF-230 and Wood Sample Weight Loss Data Compared at Different Heating Rates.

Figure 2 shows the mass concentration data which were measured at 5 and 10 W/cm^2; the 2.5 W/cm^2 test did not produce a measurable concentration at the established test conditions. As would be expected from the weight loss data in Figure 1, the 10 W/cm^2 condition produced a significantly greater concentration of particulate mass than the 5 W/cm^2 case.

The smoke particle size distribution which was obtained with the cascade impactor for the 10 W/cm^2 condition is shown in Figure 3. This instrument furnishes the distribution of particulate weight over the aerodynamic size range of 0.43 to 11 microns. The smoke is sampled continuously over the entire test time; thus, the resulting size distribution is an integrated distribution for the entire test. This type of data also gives an indication of the total particulate matter generated by each sample. The 2.5 and 5 W/cm^2 test conditions produced only trace amounts of particulate deposits on the cascade plates and thus cannot be reported. Also included in the figure are data from previous tests of wood at 5 W/cm^2. [1,4] These wood data at 5 W/cm^2 are plotted since a direct comparison of the two materials under completely smoldering conditions at 10 W/cm^2 is not possible. At the higher heating rate, wood samples experience flaming ignition early in the test, whereas the Olin RF-230 sample does not. The data in Figure 3 show that the RF-230 sample produced considerably less particulate weight per gram of sample weight than the wood generated at a lower heating rate. Both materials produced particles in approximately the same range of particle sizes with the RF-230 size distribution curve corresponding to a mass median diameter of 0.64 micrometers.

Figure 4 shows the size distribution data obtained using the Electrical Aerosol Analyzer in the test utilizing 10 W/cm^2 heat flux. This test condition produced particles with high particle concentrations below the size of one micron at the indicated test times. Reliable data is not available earlier

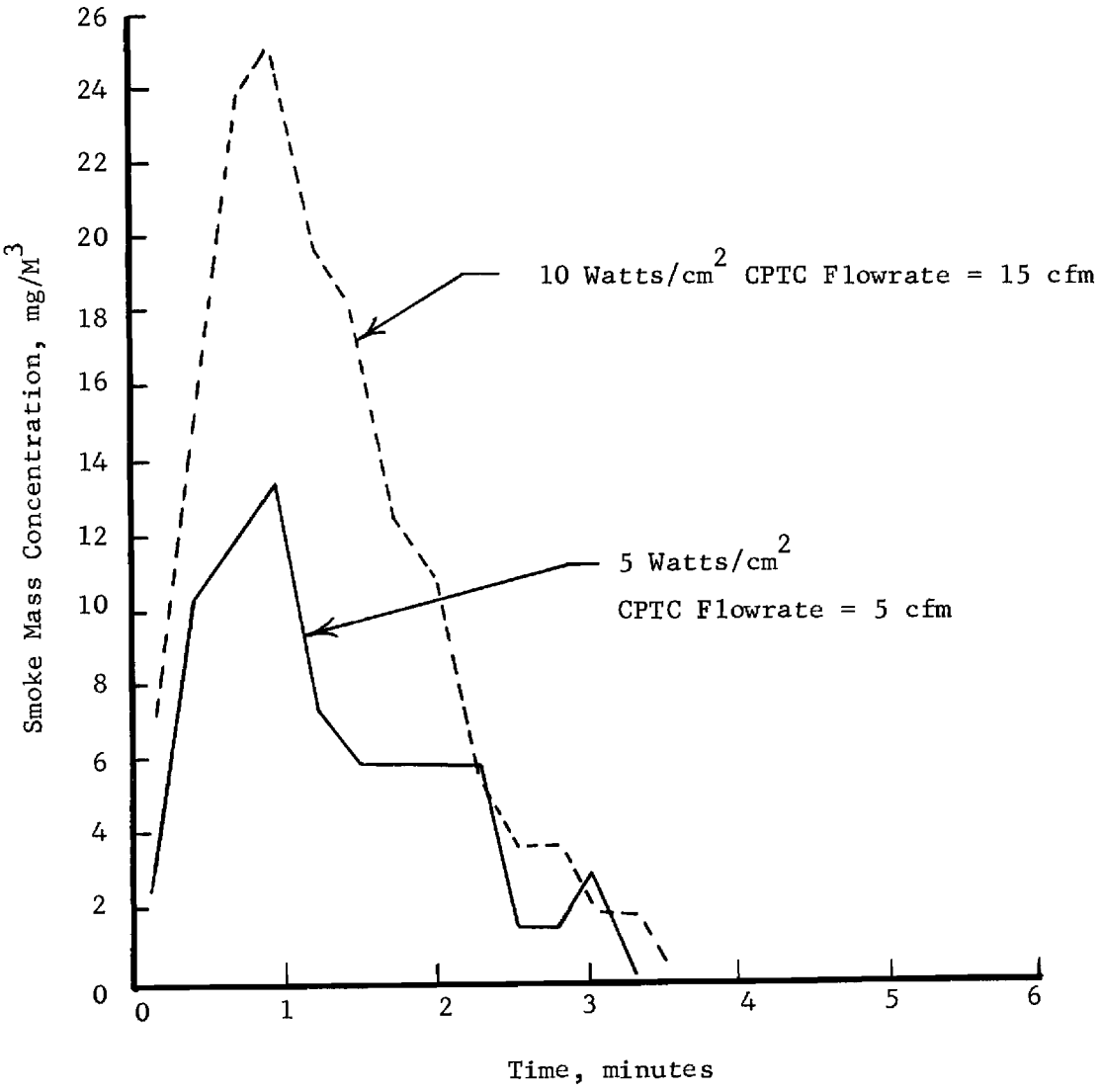


Figure 2. Time Resolved Smoke Particle Mass Concentrations Produced by Olin RF-230 at 5 W/cm^2 and 10 W/cm^2 (Nonflaming) in Room Temperature Air.

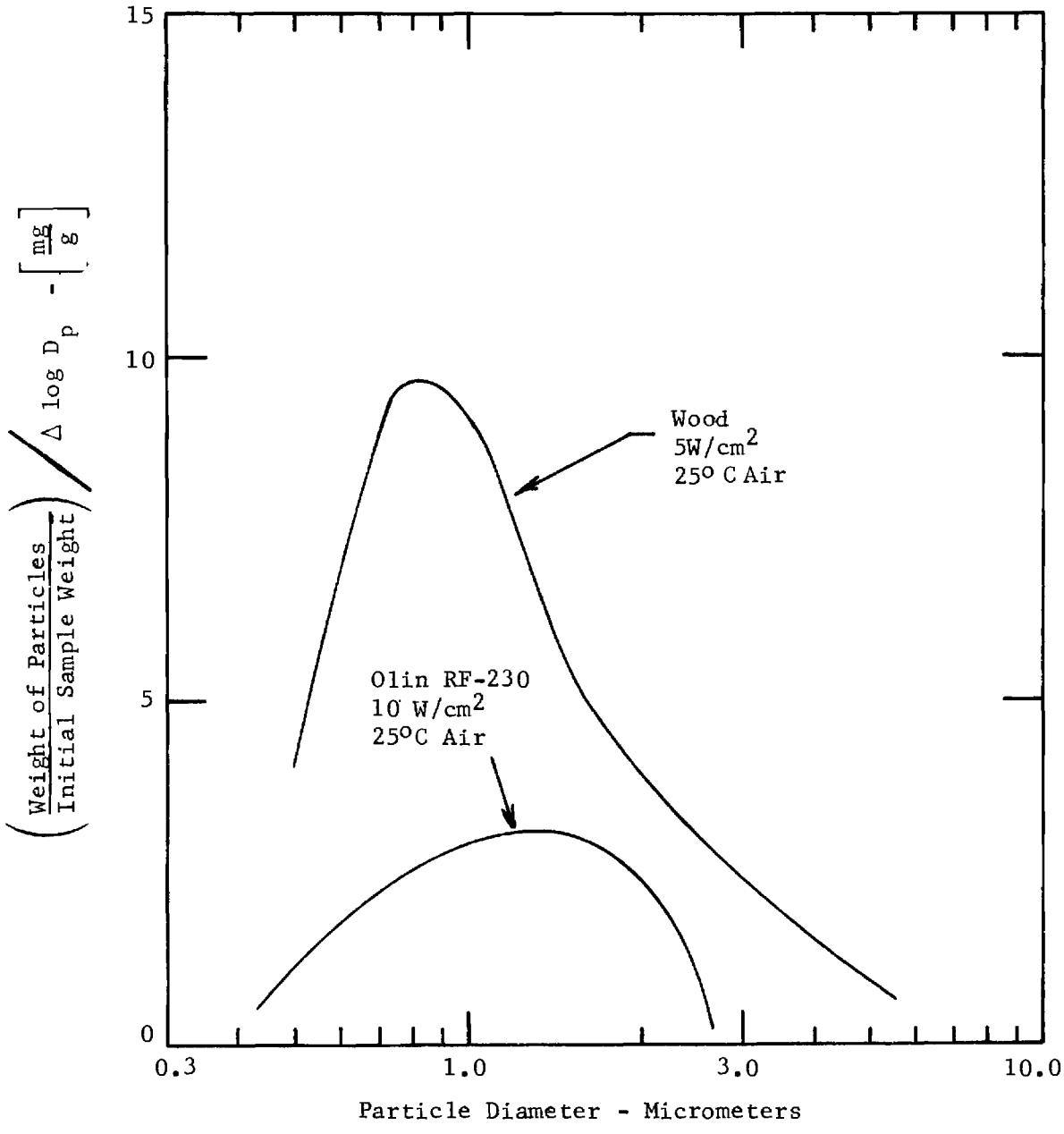


Figure 3. Comparison of Particle Size Distributions Measured for Olin RF-230 and Wood.

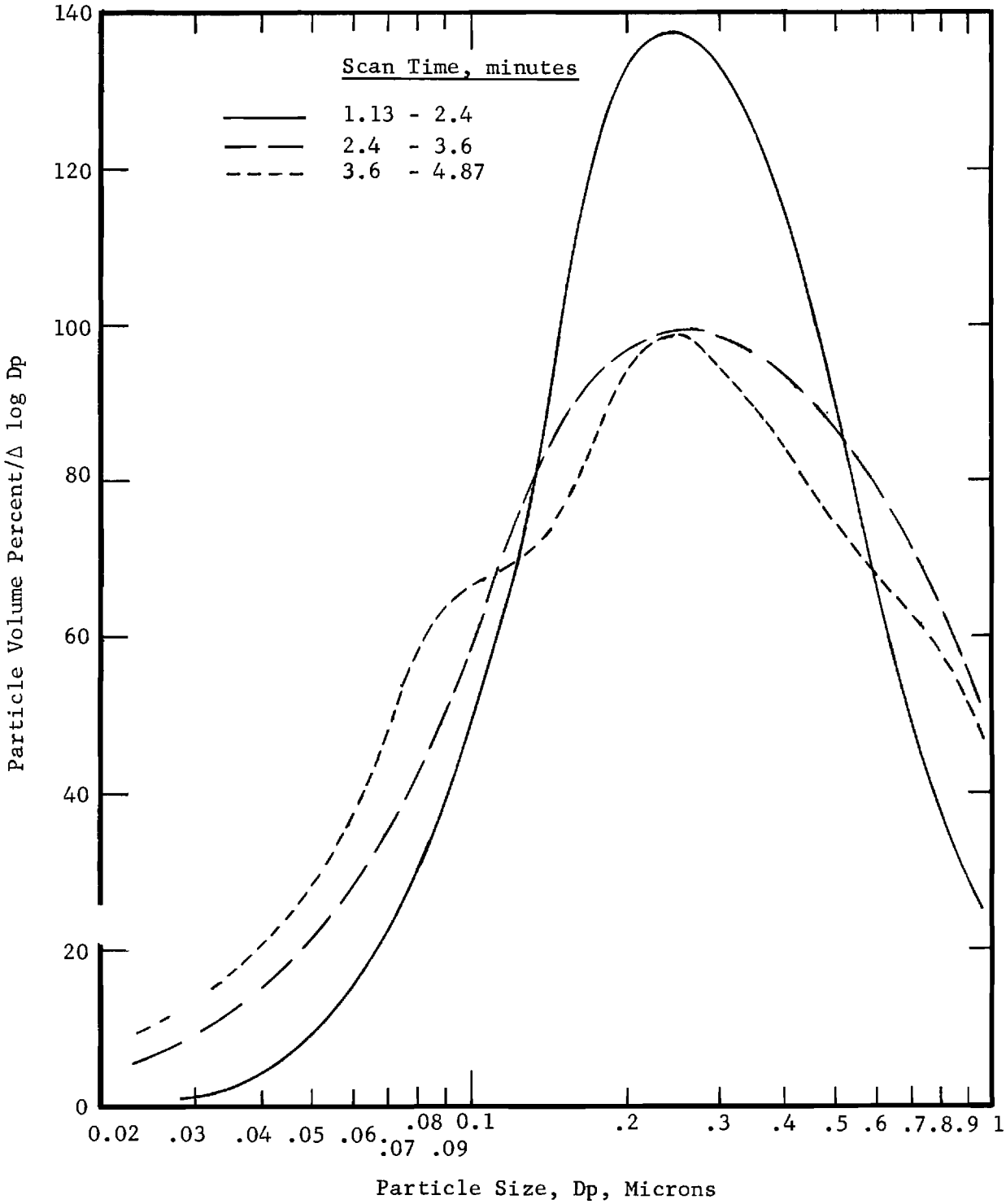


Figure 4. Particle Size Distributions Measured for Olin RF 230 Exposed to 10 Watts/cm^2 Radiant Flux and 25°C Air

in the test since in the early portions of the test the particulate concentration was increasing rapidly during the scan time. Size distributions at times later than indicated are not available because the particulate concentration was too low.

The corresponding size distribution for 10 W/cm^2 obtained with the cascade impactor which is shown in Figure 3 indicates significant particulate concentrations above one micron. However, this cascade impactor data does not contradict the EAA data since the impactor collects most of the particulate matter during the early stages of the test when the concentration is high and the particles tend to be larger.

The optical density measurements in the 25°C environmental air temperature at 5 W/cm^2 and 10 W/cm^2 are presented in Figure 5. The 10 W/cm^2 heat flux produced significantly greater optical densities than at 5 W/cm^2 while the 2.5 W/cm^2 heat flux did not produce a measurable optical density.

Figure 6 shows the variation of the average particle size during exposure of the sample to 5 and 10 W/cm^2. The average particle size during the tests is about 0.7 to 0.8 microns in both cases.

B. <u>High Temperature Tests at 2.5 W/cm^2 and 10 W/cm^2</u>

High temperature tests of Olin RF-230 rigid urethane samples have been conducted according to the test schedule outlined in Table I, and the results are reported in Figures 7 through 10. Measurements of the physical characteristics of smoke generated by smoldering samples have been taken for ventilation gas (air) temperatures of 125°C, 200°C and 300°C, while the samples were exposed to both 2.5 W/cm^2 and 10 W/cm^2 radiant fluxes. As mentioned previously, this series of tests has been limited to in situ optical system and force transducer measurements, since the aerosol sam-

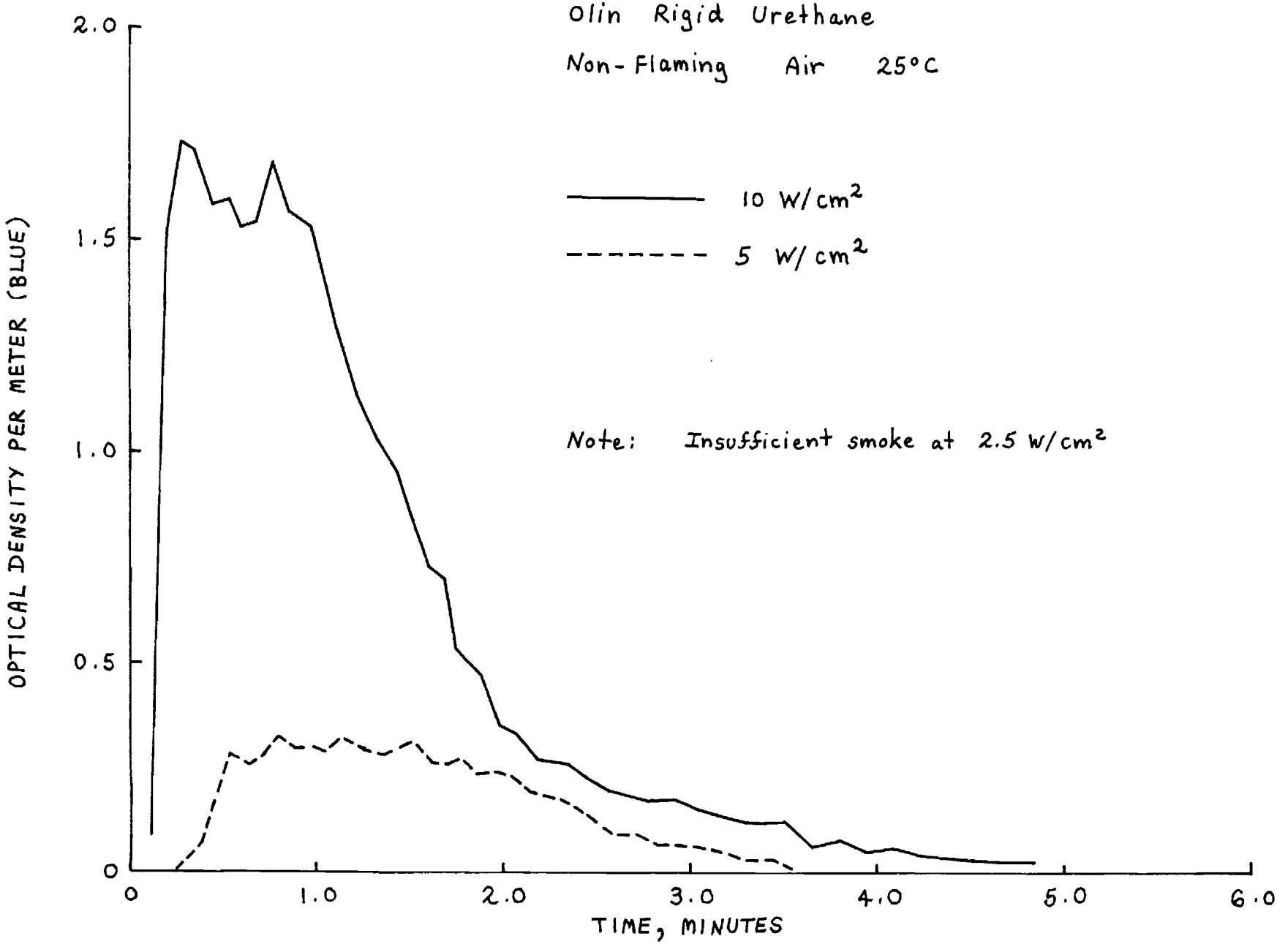


Figure 5. Time Resolved Smoke Optical Densities Produced by Olin RF-230 at 5 W/cm^2 and 10 W/cm^2 (Nonflaming) in Room Temperature Air.

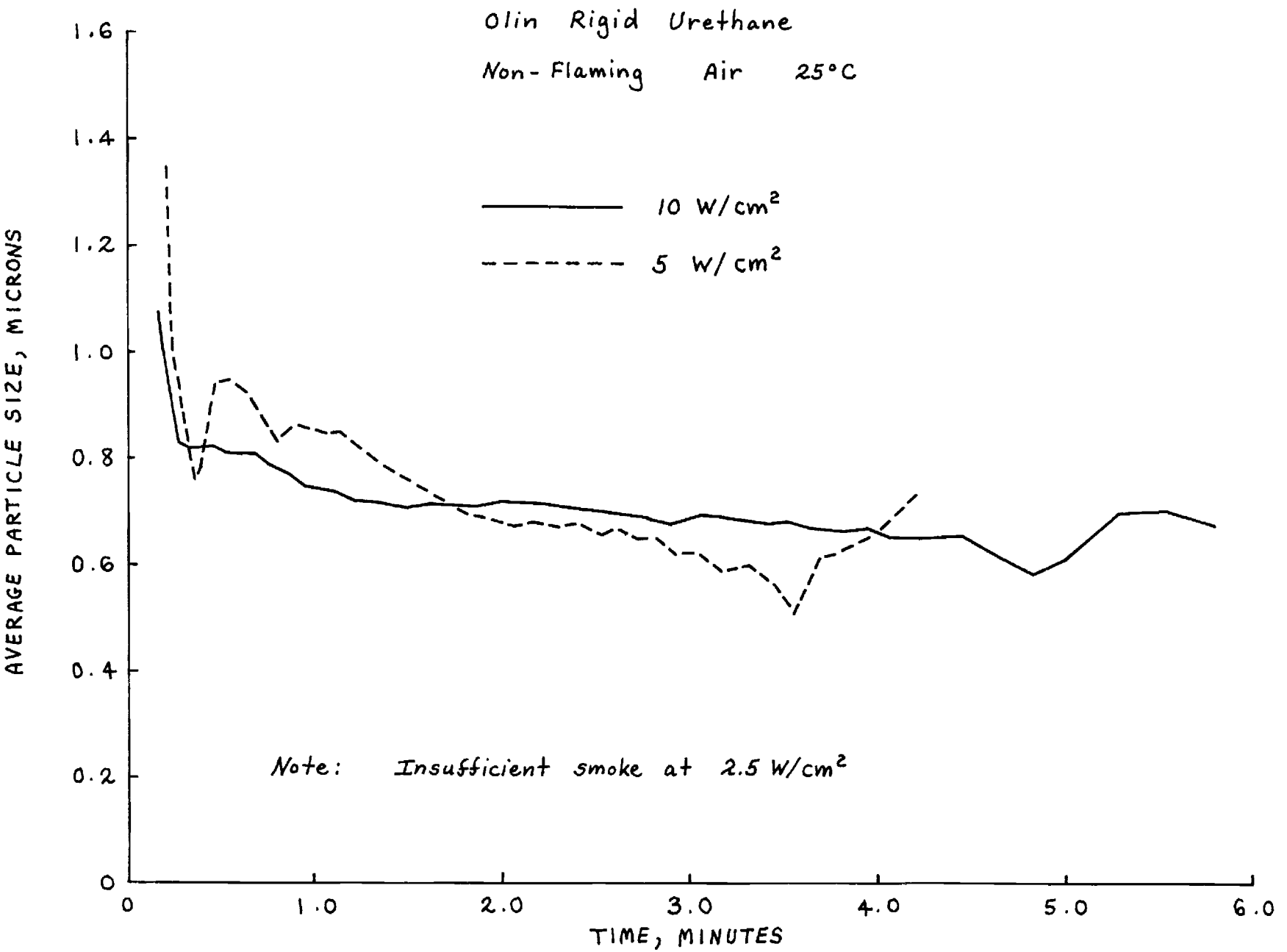


Figure 6. Time Resolved Average Smoke Particle Sizes Produced by Olin RF-230 at 5 W/cm^2 and 10 W/cm^2 (Nonflaming) in Room Temperature Air.

pling system instrumentation cannot be operated at elevated temperatures.

Figure 7 compares the weight loss data which were obtained for the high temperature environments at both 2.5 W/cm^2 and 10 W/cm^2. The 200°C data which is indicated for the 2.5 W/cm^2 case is estimated based on the initial and final sample weights for this test. In this case, the force transducer did not provide reliable data due to a combination of the relatively small sample weight loss and CPTC thermal transients. Note also that in the 300°C case at 10 W/cm^2 radiant flux, the sample sustained flaming ignition at the start of the test. These were the only tests conditions (300°C, 10 W/cm^2) in which flaming ignition was observed in this test program. The results (Figure 7) show that the effect of increasing the environmental temperature is to increase the rate at which the sample is pyrolyzed and loses weight. At 2.5 W/cm^2 the effect of increasing the temperature is slight up to 200°C, however the 300°C environment results in a substantial increase in the weight loss rate. For the 10 W/cm^2 tests, the weight loss rate is accelerated between 25°C and 125°C, whereupon little additional effect is observed as the temperature is increased from 125°C to 300°C.

Figures 8 and 9 describe the time dependence of the smoke particle mean diameter, D_{32}, measured for the rigid urethane samples at all ventilation gas temperatures under consideration for the 10 W/cm^2 flux (Figure 8) and at 300°C only for the 2.5 W/cm^2 flux (Figure 9). Data is not reported at 25°C, 125°C and 200°C in the 2.5 W/cm^2 case, since the smoke concentrations were too low to be measured by the in situ optical system. The measurements shown in Figure 8 for 10 W/cm^2 tests indicate that the average particle size stabilized between 0.6 and 0.8 micrometers after the initial starting transient for all ventilation gas temperatures. Fur-

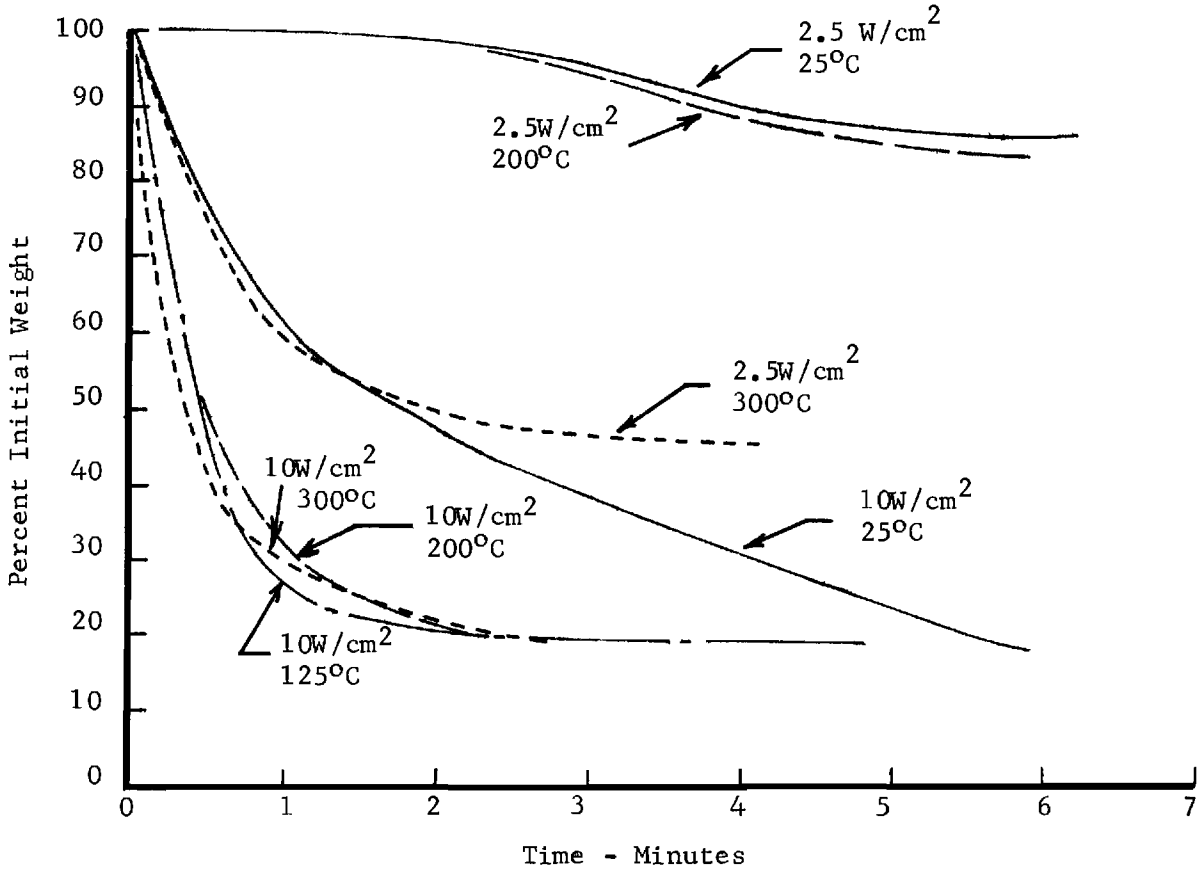


Figure 7. Olin RF-230 Sample Weight Loss Data Compared at Several Environmental Temperatures.

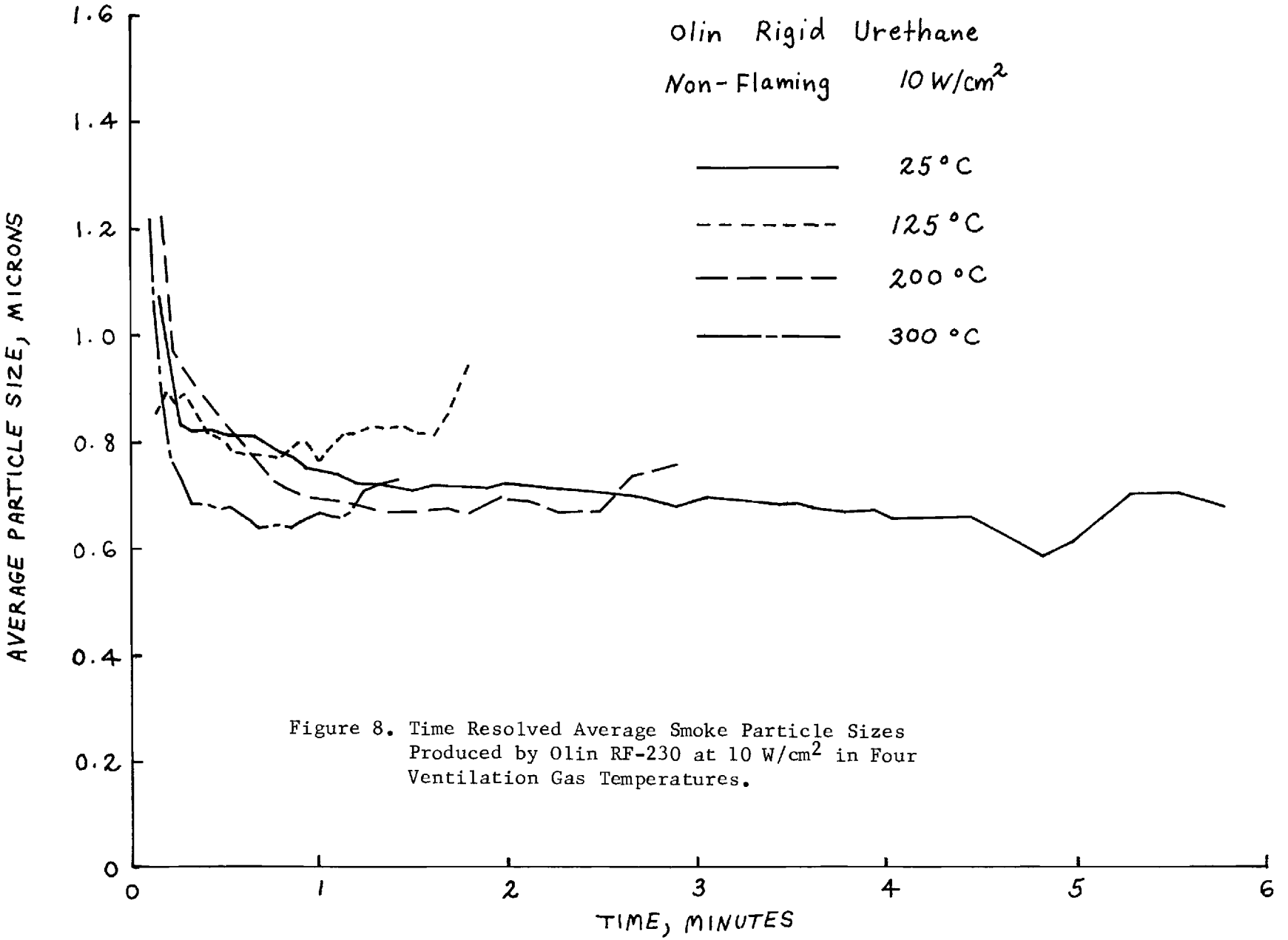


Figure 8. Time Resolved Average Smoke Particle Sizes Produced by Olin RF-230 at 10 W/cm^2 in Four Ventilation Gas Temperatures.

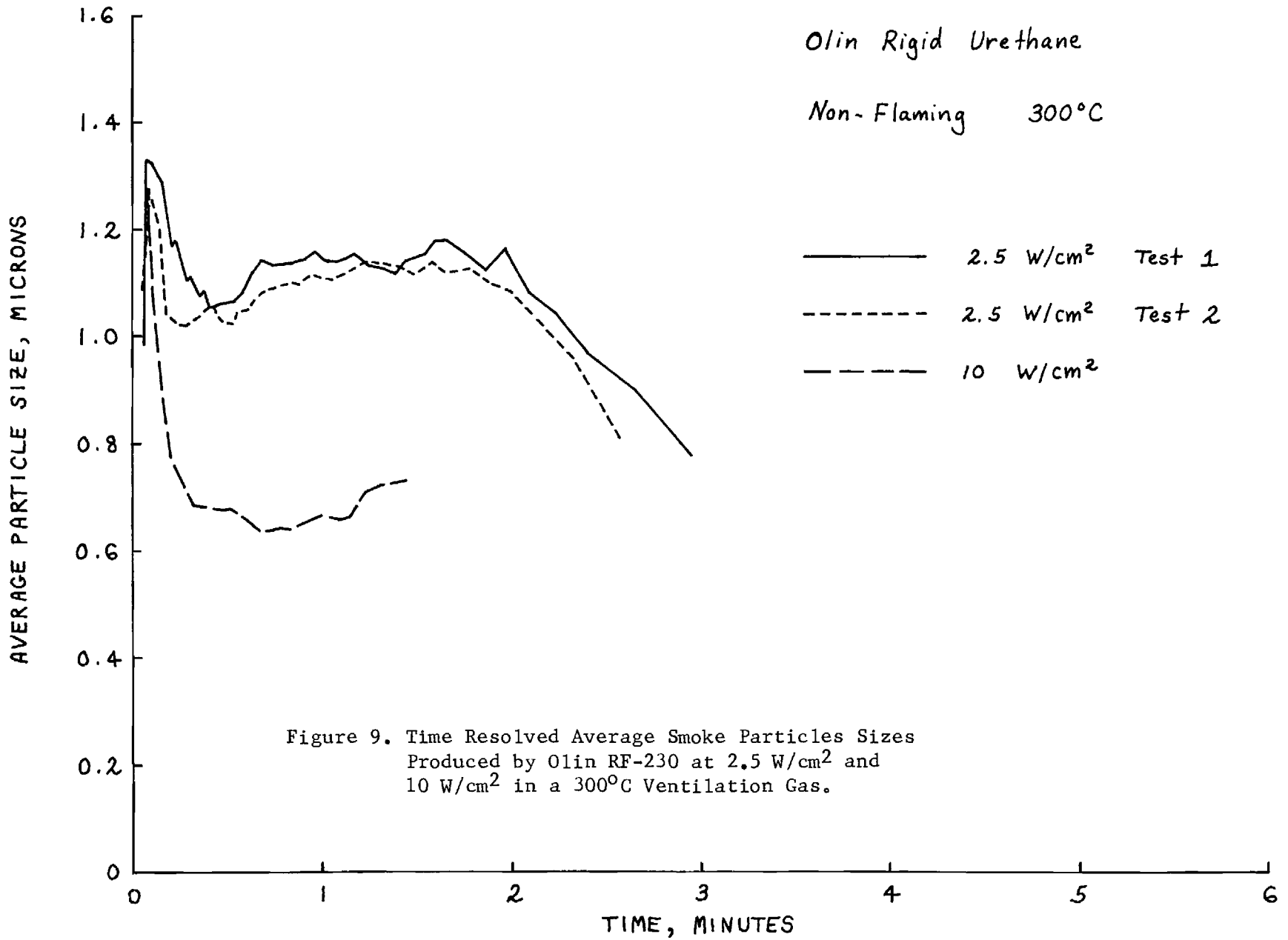


Figure 9. Time Resolved Average Smoke Particles Sizes Produced by Olin RF-230 at 2.5 W/cm^2 and 10 W/cm^2 in a 300°C Ventilation Gas.

thermore, the flaming case (300°C, 10 W/cm^2) produced the smallest particles earlier than the other tests at 10 W/cm^2. Figure 9 illustrates the fact that the 2.5 W/cm^2 (at 300°C) case generated the largest particle sizes of any of the other test conditions considered for which measurements could be taken. A relatively stable period is observed when the average particle sizes are found to be between 1.0 and 1.2 micrometers, where these results are clearly repeatable for the two tests plotted. These particle sizes are considerably larger than those measured in all 10 W/cm^2 tests and the 300°C test is plotted on Figure 9 for purposes of comparison.

Smoke optical density measurements shown in Figure 10 indicate that increasing the ventilation gas temperature from 25°C to 300°C with a radiant heat flux of 10 W/cm^2 has the effect of reducing overall optical density levels for each environmental temperature increase. This is consistent with results obtained in tests of a series of flexible urethane foams.[5] Optical density results are also plotted in Figure 10 for the only 2.5 W/cm^2 test that produced measurable quantities of smoke.

C. Summary

In the low temperature nonflaming tests of Olin RF-230 rigid urethane foam at 2.5, 5 and 10 W/cm^2 radiant fluxes, sample weight loss measurements show that the samples decompose faster and that a lesser fraction of the initial sample weight remains at the end of a test as the heating rate increases. Also, the 10 W/cm^2 condition produced greater concentrations of particulate mass and higher optical density levels than the lower heating rates. Cascade impactor data show that the RF-230 foam generates less total mass of particulates than wood samples produce per gram of

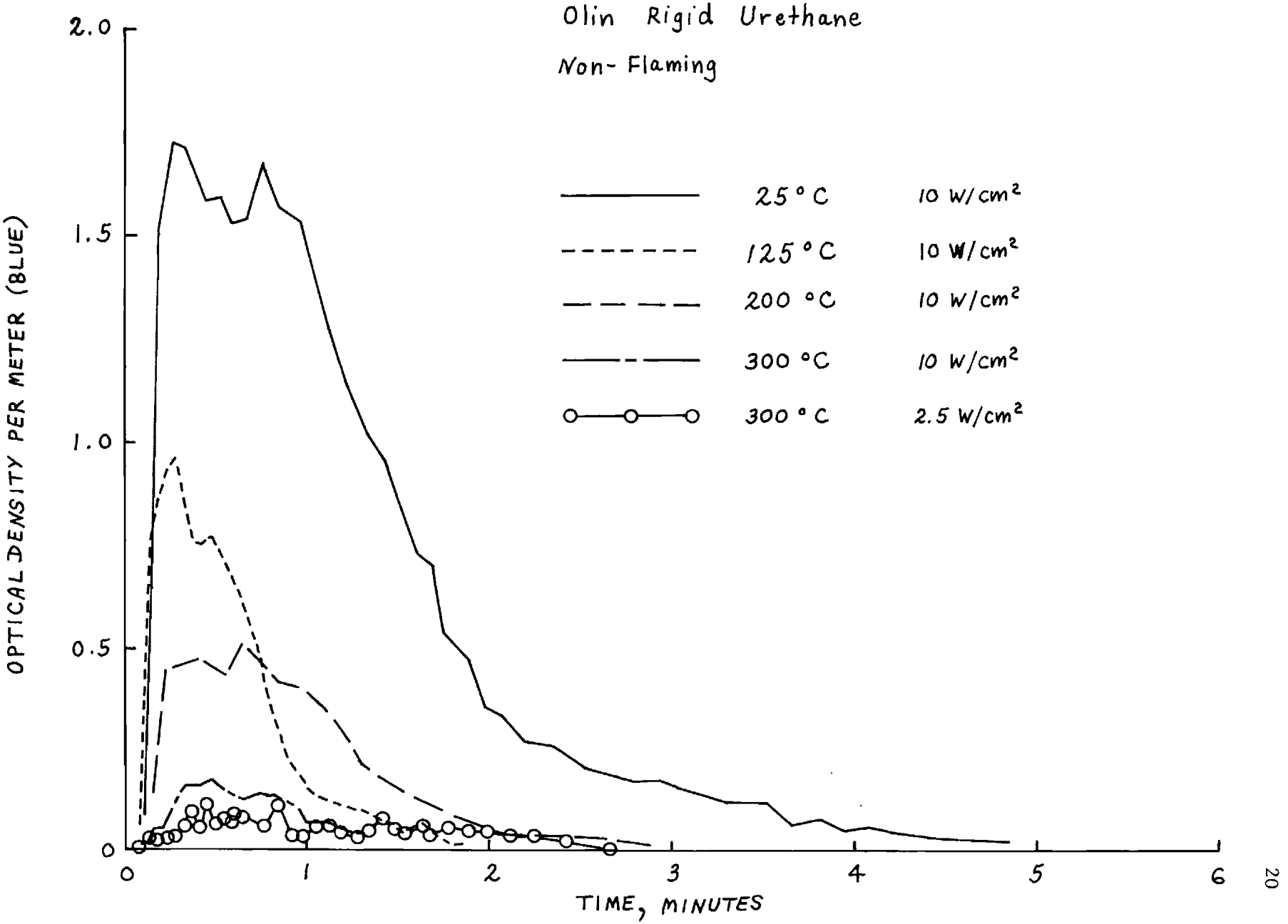


Figure 10. Time Resolved Smoke Optical Densities Produced by Olin RF-230 at 2.5 W/cm^2 and 10 W/cm^2

initial sample weight when compared under completely nonflaming conditions. Particle sizes are found to be nearly the same in both the 5 W/cm^2 and 10 W/cm^2 cases, where most particles are found in the range of about 0.4 to 4 micrometers.

Nonflaming tests of the 01in RF-230 foam in atmospheric temperatures up to 300°C at 2.5 W/cm^2 and 10 W/cm^2 radiant fluxes provide data that show that, in general, the effect of increasing temperature is to increase the pyrolysis rate (and weight loss) rate of the samples. In the case of tests characterized by a 300°C temperature and a radiant flux of 10 W/cm^2, the sample sustained immediate flaming ignition at the start of the tests. For tests conducted at 10 W/cm^2 in all environmental temperatures considered, mean particle sizes were generally between 0.6 and 0.8 micrometers; however, the test at 2.5 W/cm^2 in a 300°C atmosphere produced particles between 1.0 and 1.2 micrometers in diameter. Finally, maximum optical densities at 10 W/cm^2 are considerably reduced as the environmental temperature is increased. These results indicate that the smoke particulates generated under nonflaming conditions are probably predominantly composed of condensible liquid pyrolysis products; since the nucleation and/or condensation processes would be considerably retarded at the higher temperatures.

V. CHEMICAL ANALYSIS OF VOLATILE COMPONENTS OF POLYURETHANE SMOKE PARTICULATES

The chemical analysis program has been concerned with the identification of volatile compounds absorbed onto the particulates generated from the nonflaming combustion of a rigid polyurethane foam sample (Olin RF-230). The volatile compounds selected for particular attention have been those with high inherent toxicity, and which might be expected to be present in the sample smoke (including HCN and low molecular weight aldehydes). The interest in these toxic compounds has arisen because it has been established that particles of $< 0.3\mu m$ diameter readily bypass body defenses, penetrating deep into the alveolar region of the lung, and could thus act as carriers of acutely toxic substances into the blood stream. Clearly, in most fire situations direct exposure to high concentrations of CO, etc, will be a primary cause of death. However, many instances of delayed pulmonary edema have been observed after exposure to minor fires, or after exposure to the scenes of already extinguished fires. In an attempt to see if any chemical evidence of a possible toxic hazard involving particulate transport of volatiles could be observed, the present work was carried out. The work by Stone[6,7] has shown that significant amounts of HCl can be carried by particulates generated from PVC combustion, and so it might be anticipated that polyurethane samples would behave similarly for HCN, acrolein etc. Initial sampling of CO and CO_2 from the gas stream was abandoned at the suggestion of the Olin Corporation, when no significant concentrations of CO were detected by gas chromatography.

A. Trapping

In order to design a simple, effective and versatile trapping system, a solid absorbant (Porapak R) was selected in preference to cold traps or liquid traps. Collected material was readily released from this trap by heating to 180°C and flushing with He for 8 min. A repetition of this procedure showed that virtually all collected material was released by a single heating cycle.

B. Operating Procedure

1. The polyurethane sample was burned under non-flaming conditions in the ventilated combustion products test chamber at 10 W/cm^2 radiant flux. An air flow of 142 liters per minute was used when samples were collected for chemical analysis. The sample was burned for 30 sec before sampling was initiated.

2. Particulates were sampled at 28 liters per minute flow, with a probe connected to a vacuum pump, and collected on a glass fiber filter (Gelman) of 47 mm diameter (Figure 11). Collection for 3 minutes gave approximately 35.5 mg of particulate sample.

3. The filter and holder were sealed off, removed from the collection line, and connected into a trapping system (Figure 12).

4. The filter and holder were then heated to 40°C, a stream of dry He passed through the filter at 12 ml/min, and the volatiles collected on a short (10cm) trap of Porapak R (80/100 mesh). The filter temperature was raised to 80°C and maintained at that value for 1 hour. A total collection time of 80 minutes was used.

5. In order to introduce the sample to the GC column, the trap was closed off, and connected to a releasing/injection system (Figure 13). The GC baseline was set with the carrier gas in its normal path (a), then

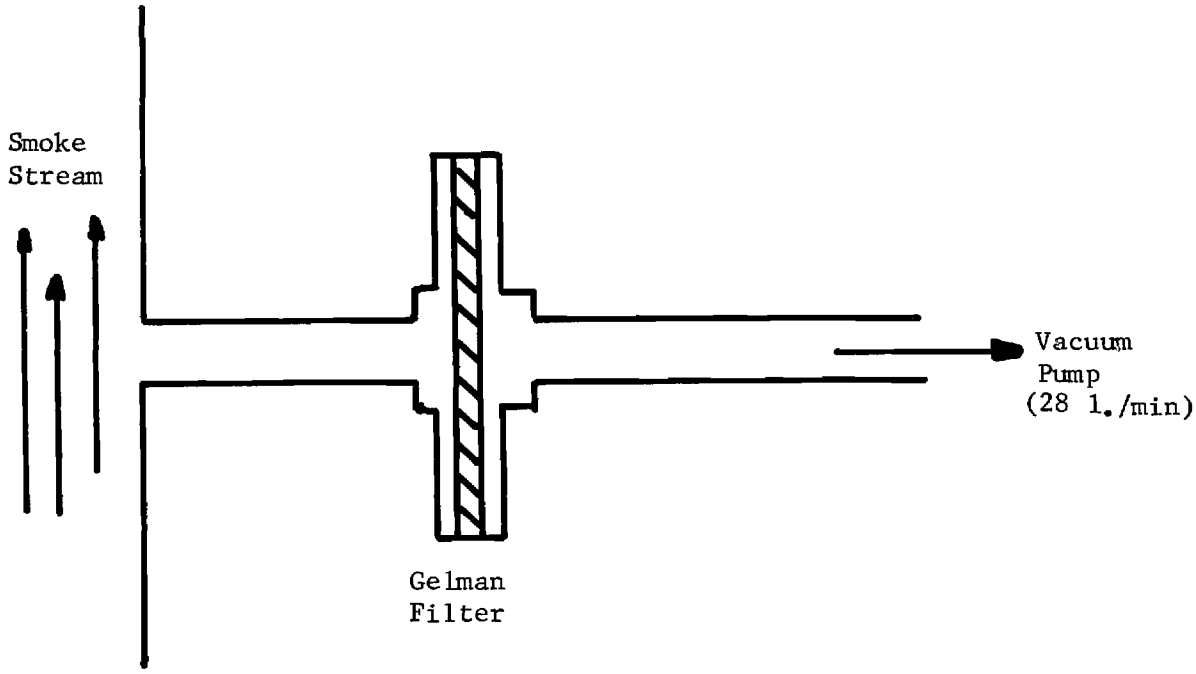


Figure 11. Smoke Particulate Collection Apparatus.

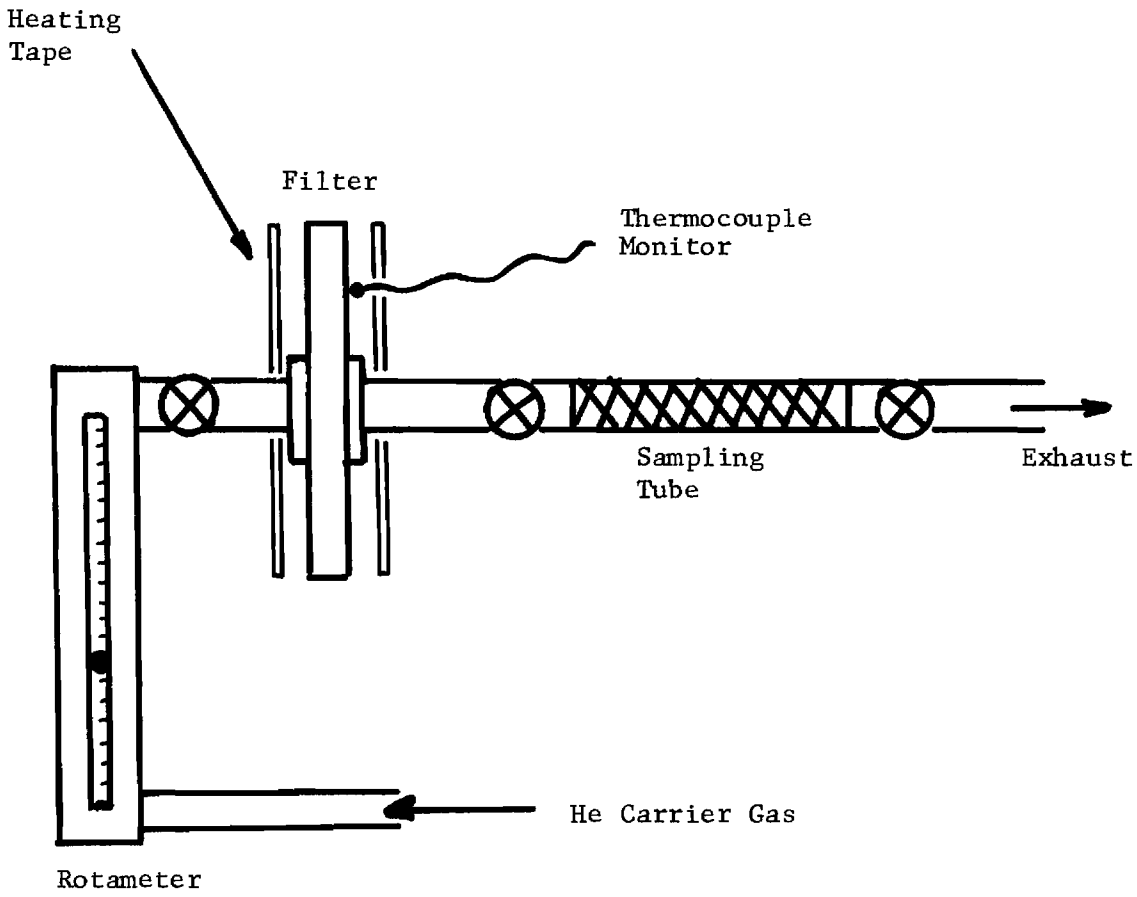


Figure 12. Trap for Volatiles Released from Particulates.

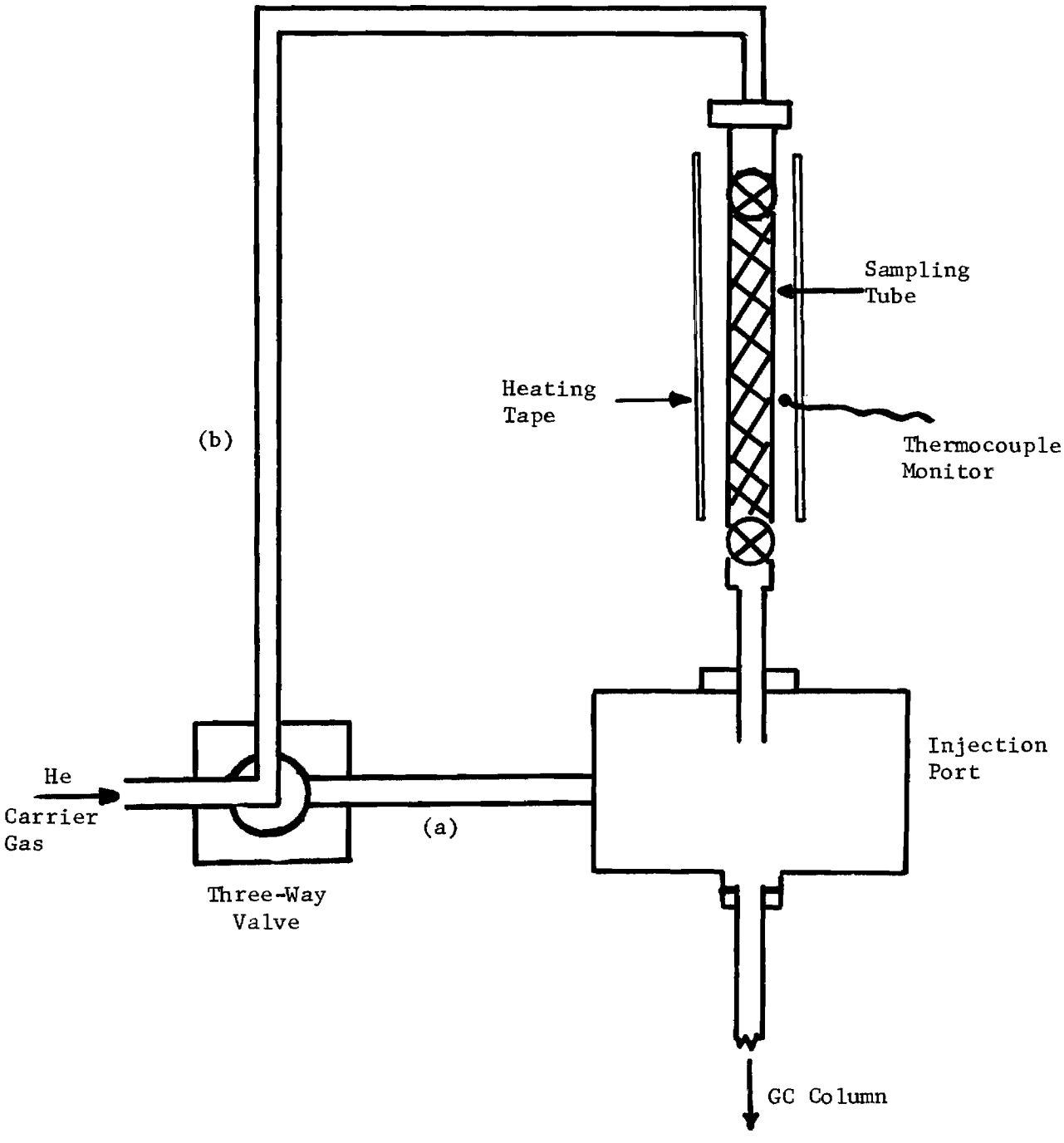


Figure 13. Trap Release, and Injection System.

the three-way valve directed the flow through the sampling tube via path (b). The sampling tube was heated to 180°C for 8 minutes, and the volatiles desorbed from the trap and collected onto the cool (70°C) front end of the analytical GC column.

6. Gas chromatographic separation used Porapak R columns (80/100 mesh, 2 meters x 3.2 mm. id glass column). The chromatograms were run isothermally at 70°C for 20 minutes, then temperature programed at 8°C per minute up to a maximum of 220°C. Gas chromatographs used were Hewlett-Packard Models 5720A (thermal conductivity detector) and 5711A (FID detector).

C. Results and Discussion

Gas chromatographic traces of the polyurethane sample (Figure 14), using an FID detector, showed approximately 18 well resolved, and many more partly resolved peaks. In an attempt to obtain identification of these peaks, the Hewlett-Packard 5930A Dodecapole Mass Spectrometer was used, together with its library of mass spectral data files. Unfortunately, it was found that the Porapak R showed considerable bleeding (see Figure 14) which made identification of only the major peaks possible. The total ion chromatogram (Figure 15) shows major peaks from acetone, acetic acid, and either cyclohexane, methylcyclohexane or methylcyclopentanone.

As no positive identification of HCN or low molecular weight aldehydes was achieved with the GC/MS system, identification was attempted using a gas chromatograph with thermal conductivity detector in order to obtain a response for HCN. Standard amounts of HCN and acrolein were injected for standardization purposes. Figures 16 and 17 show the chromatograms. Comparison of GC traces for the polyurethane sample using the thermal conductivity detector showed no detectable amounts of either HCN or acrolein.

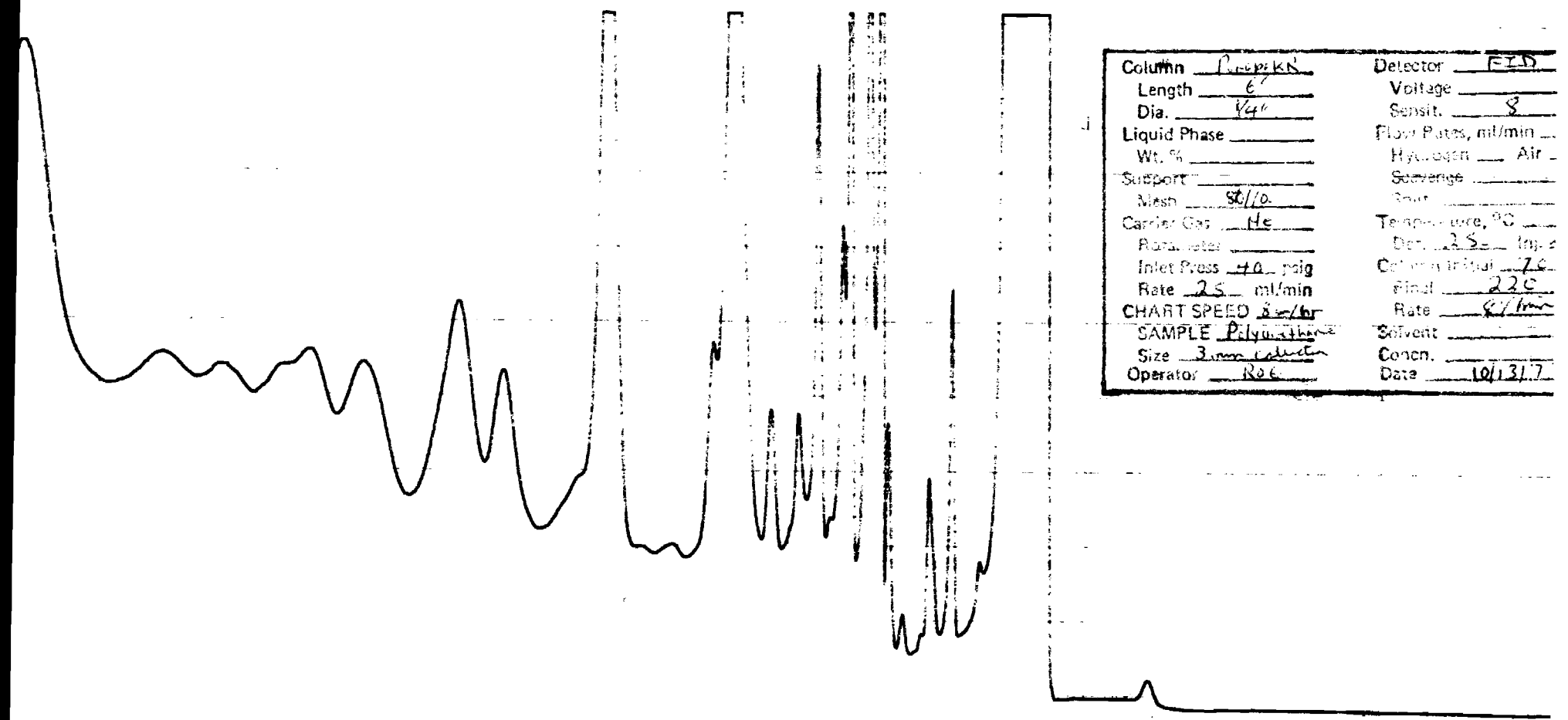


Figure 14. Chromatogram of Polyurethane Volatiles; Porapak R Column, FID Detector.

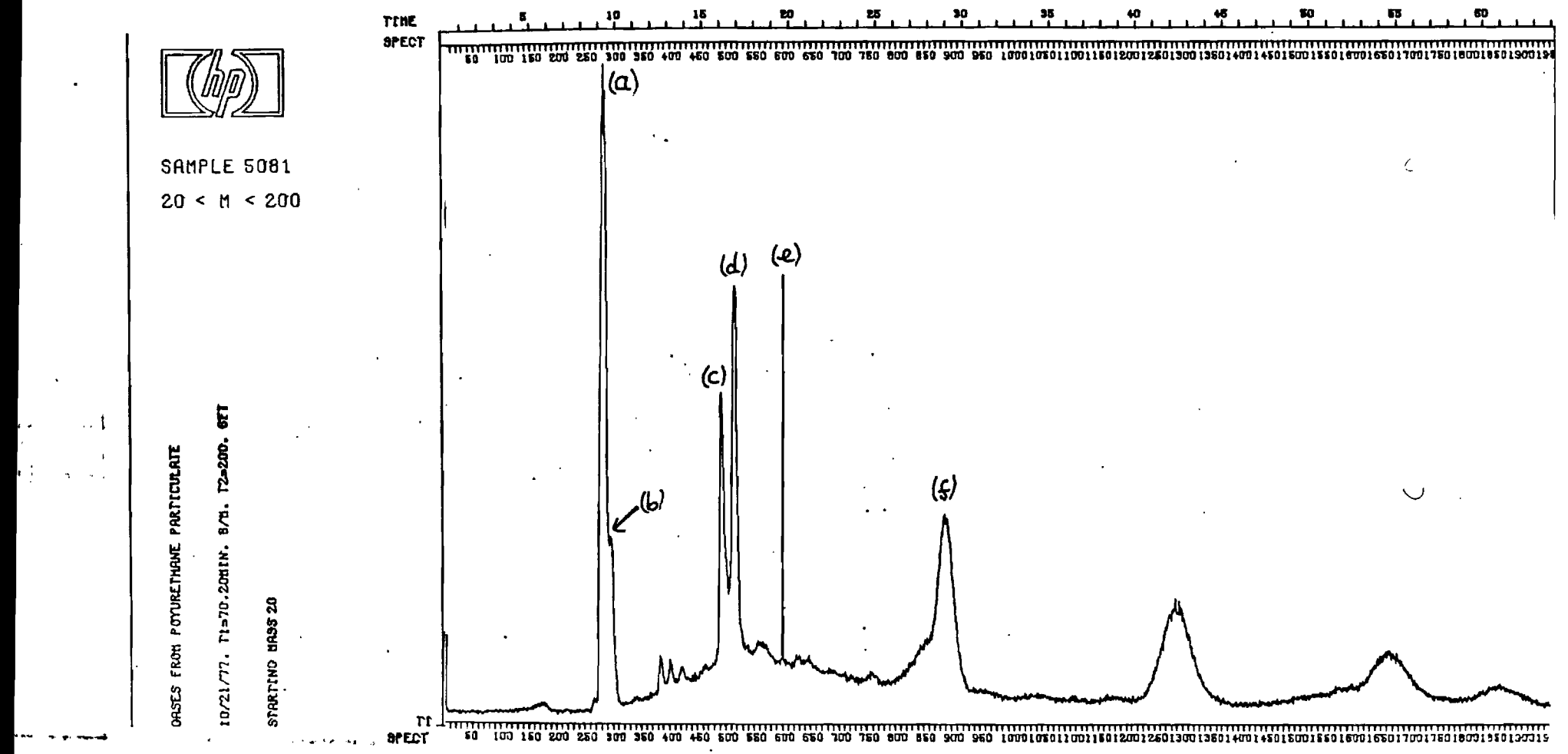


Figure 15. Total Ion Chromatogram of Polyurethane Particulate Volatiles; (a) Acetone (b) Carbon Disulfide? (c) Acetic Acid (d) Chloroethanol? (e) Instrumental Artifact (f) Cyclohexanone, Methylcyclohexane or Methylcyclopentanone.

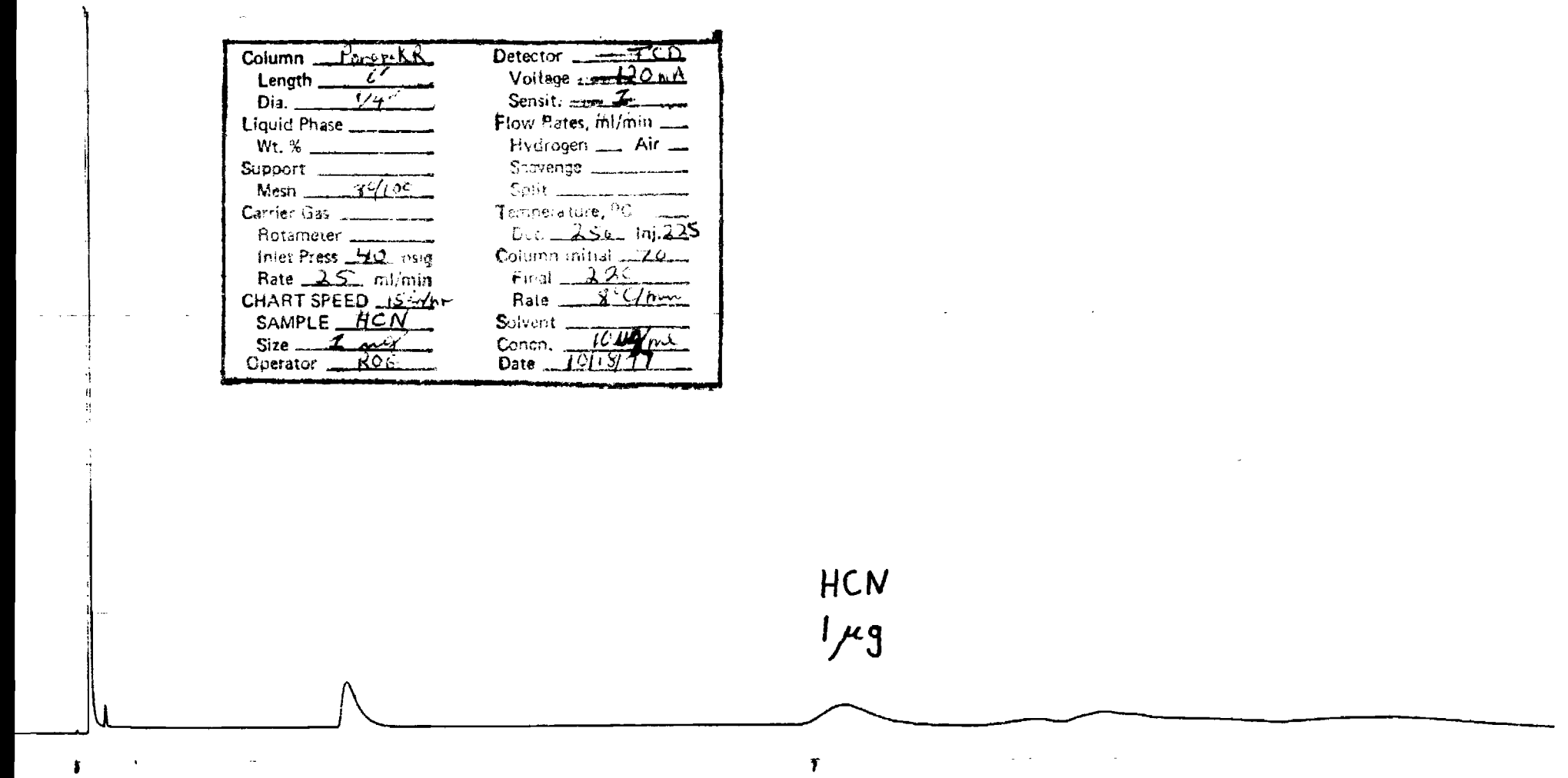


Figure 16. Gas Chromatogram of Standard HCN Gas Mixture, Porapak R Column, Thermal Conductivity Detector.

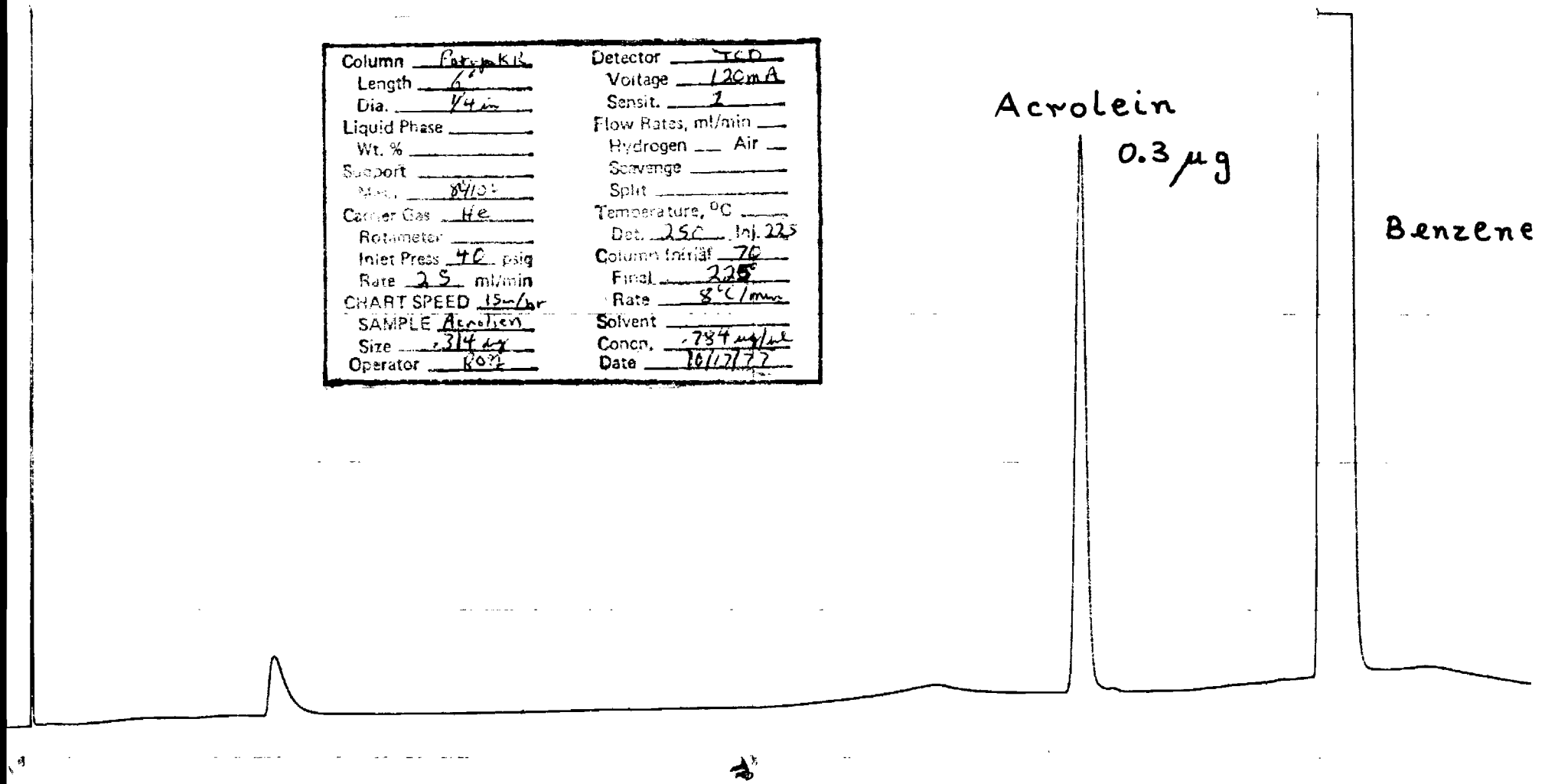


Figure 17. Gas Chromatogram of Standard Acrolein Sample; Porapak R Column, Thermal Conductivity Detector.

Consequently it may be concluded that with the system of combustion, collection and separation used, HCN is present in the collected particulates at less than 30 $\mu g/g$ of particulates.

If one assumes an average particle mass concentration of 10 mg/M^3, then 1 M^3 of smoke laden air is capable of releasing 3×10^{-2} μg HCN, resulting in an HCN concentration in the gas phase of 3×10^{-2} $\mu g/M^3$. This assumption does not, however, take into account the different mechanisms of inhalation, which could make HCN absorbed onto smoke particulates a greater hazard than simple gaseous HCN.

The GC trace for volatile compounds released from particulates collected from a wood sample is shown in Figure 18 for comparison purposes. The collection/trapping system was identical to that used for the polyurethane sample.

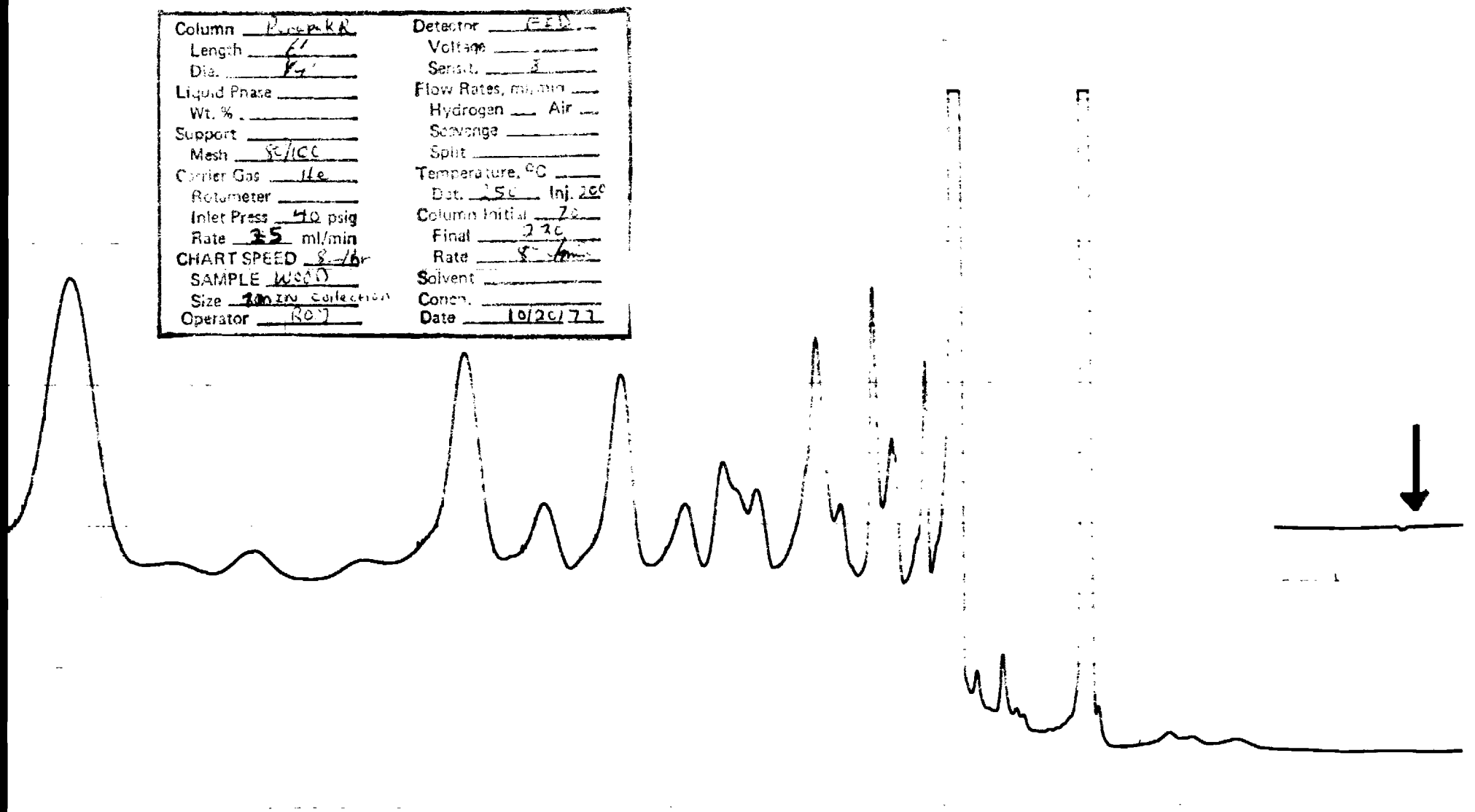


Figure 18. Gas Chromatogram of Wood Volatiles;
Porapak R Column, FID Detector.

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